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G. GRÜNER
A. ZAWADOWSKI

MAGNETIC IMPURITIES IN NON-MAGNETIC METALS

Hungarian Academy of Sciences

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G. Grüner
Imperial College, Department of Physics, London
and
Central Research Institute for Physics, Budapest, Hungary+

and

A. Zawadowski
Central Research Institute for Physics, Budapest, Hungary+
and
Institut Laue-Langevin, Grenoble, France

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+Permanent address

ABSTRACT

The paper summarizes the properties of 3d transition metal impurities in simple metal hosts.

The microscopic models of Friedel, Anderson and Wolff are reviewed and the question of the formation of the magnetic moment on the impurity is shortly discussed. The structure of the Anderson model in the Hartree-Fock approximation and the correlation effects in the weekly magnetic limit when the Coulomb correlation energy u is smaller than the width Δ of the d-states is summarized together with the perturbational treatments of the model in the strongly magnetic limit $u/\Delta >> 1$.

The s-d exchange model and the Kondo effect /the logarithmic increase of the resistivity with decreasing temperature/ is discussed and the various approximations of this model are contrasted with each other. The relation between the Anderson and s-d exchange model is derived and the nature of the Schrieffer-Wolff transformation is analyzed, in particular the question of the polarization of the s and d states.

The experimental status of affairs is reviewed next, and the experimental data obtained mainly on alloys of noble metals and aluminium with 3d elements are collected to answer the questions raised in the previous chapters. Experimental evidences on the singlet ground state, charge neutrality and on the single particle and many-body resonances are summarized. The question of the validity of the various approximations of the models is answered by comparing the experimentally found behaviours with theoretically derived formulas this comparison leads to the basic unresolved questions in this field.

Finally the latest developments in the theory is reviewed. These theories consider the Kondo problem as a typical case of the infrared divergencies, and are based on scaling and renormalization group techniques, they may bridge the gap between the earlier theories and the experimental facts.

РЕЗЮМЕ

В работе изложены основные свойства переходных металлических примесей типа 3d в простых металлических матрицах.

Рассматривается модель Фриделя, Андерсона и Вольфа и кратко обсуждаются условия образования магнитных моментов примесей.

Рассматривается математическая структура модели Андерсона в приближении Хартри-Фока, корреляционные эффекты в слабом магнитном пределе, когда корреляционная энергия Кулона /U/ меньше чем ширина d-состояний /Δ/, а также методом возмущения случай сильного магнитного предела, когда $U/\Delta >> d$.

Обсуждается s-d обменная модель и эффект Конда /логарифмический рост сопротивления с понижением температуры/ и сравнены друг с другом разные математические приближения модели. Получается явное соотношение между моделями Андерсона и s-d обменной моделью и анализируется поведение трансформации Шриффера-Вольфа, уделяя внимание вопросу поляризации состояний s и d.

В последствии рассматривается современное положение этих проблем с точки зрения экспериментов. Собраны экспериментальные данные для сплавов из благородных металлов и для алюминия с 3d-элементами, а также данные в подтверждение таких вопросов как синглеттное основное состояние, электрическая нейтральность и одно- и многочастичный резонанс.

Проблема применимости разных приближений теорий решена сопоставлением экспериментальных данных с теоретическими результатами. Это сравнение дает возможность сформулировать некоторые фундаментальные и пока не решенные проблемы этой области.

В заключение рассматриваются самые новые результаты теории. Эти теории считают эффект Конда типичным примером инфракрасной расходимости, они применяют методы ренормированных групп и масштабной инвариантности. Эти теории могут устранить расхождение между результатами настоящей теории и экспериментальными данными.

ÖSSZEFOGLALÓ

A cikk az egyszerü fémekben oldott 3d átmeneti fém szennyezések tulajdonságaival foglalkozik.

A Friedel, Anderson és Wolff által kidolgozott mikroszkópikus modelleket és a szennyezés helyén fellépő mágneses momentum megjelenését tárgyaljuk. Vizsgáljuk az Anderson-modell Hartree - Fock közelitését és korrelációs effektusokat a gyengén mágneses határesetben, amikor a Coulomb korrelációs energia U kisebb mint a d-állapotok szélessége Δ, valamint a modell perturbációs közelitését az erősen mágneses limitben, amikor $U/\Delta >> 1$.

Az s-d kicserélődési modellt és a Kondo effektust /az ellenállás logaritmikus növekedése csökkenő hőmérséklettel/ tárgyaljuk és összehasonlitjuk a különböző közelitéseket. Az Anderson és s-d modell kapcsolatát vezetjük le és a Schieffer-Wolff transzformációt analizáljuk, különös tekintettel az s és d állapotok polarizációjára.

Ezután a kisérleti viszonyokat foglaljuk össze, és az átmeneti fémek nemesfémekkel és aluminiummal alkotott ötvözetein végzett kisérleteket tárgyaljuk az előző fejezetekben felvetett kérdések megválaszolására. A szinglett alapállapot, töltéssemlegesség, valamint az egyrészecske és többrészecske rezonanciák kisérleti evidenciáival foglalkozunk. A különböző közelitések érvényességének kérdését válaszoljuk meg a kisérletileg megfigyelt viselkedések elméleti kifejezésekkel való összehasonlitásával, ez az összehasonlitás elvezet a főbb meg nem válaszolt kérdésekhez.

Végül az elmélet legutóbbi fejleményeit foglaljuk össze. Ezek az elméletek a Kondó-problémát mint az infravörös divergenciák egy esetét tekintik, és főleg skála- és renormalizációs csoport közelitéseken alapulnak, ezek szolgáltathatják az átmenetet a korábbi elméletek és a kisérleti tények között.

Contents

INTRODUCTION

The subject of magnetic impurities in nonmagnetic metals includes a rather wide range of alloys, the host can be a simple metal like copper or aluminium or a transition metal like palladium, impurities with an unfilled d or f shell belong to this cathegory. The great variety of different alloys leads naturally to videly diverging physical phenomena, and different models to account for these observations. We do not survey all of them, but merely confine ourselves to simple but rather interesting cases where a strong correlation between theory and experiment is most promising: we discuss the situation where a 3d transition metal impurity is imbedded into a simple (free electron like) metal.

The first experiments date back to the early thirties, when a resistance minimum was found in certain pure metals at low temperatures, it became clear only much later that this effect is caused by a small amount of magnetic impurities. The term "magnetic" here derives from the susceptibility measurements, which show a Curie-Weiss behaviour in these cases. Impurities which have a temperate independent Pauli susceptibility do not cause such drastic effect in the resistivity. As usually a rather small amount of impurities can lead to well observable anomalies,

metallurgical factors played a crucial role.

Nuclear magnetic resonance and electron spin resonance experiments have brought the question of polarization caused by magnetic field as well as of the dynamical properties of the impurities in the limelight. A simple model was constructed to account for the experimental observations, in this so called $s\text{-}d$ model the impurity is represented by a spin operator with momentum $\sqrt{S(S+1)}$ this spin interacts with the conduction electrons through an exchange interaction $\mathcal{J}$. This interaction is weak, the dimensionless coupling constant $\mathcal{J}\rho_0(E_F)$, where $\rho_0(E_F)$ is the density of the host conduction electron states at the Fermi level, is of the order of o,1. Due to this weak interaction perturbation treatment was expected to work and to give reasonable answers to questions like polarization, resistivity, specific heat, etc. The main interest was focused to impurity-impurity interactions, which play an important role even for concentrations as small as one atomic percent.

An other line of approach attempted to give answer to the question of the existence of magnetic moment on the impurity. Friedel has first adressed himself to solve this problem using scattering theory; the models of Anderson and Wolff rely heavily on Friedels arguments. For single impurities the mean field approximation of the models was succesful in di-

viding the impurities to magnetic and nonmagnetic according to the ratio of two parameters, the Coulomb correlation energy U and the width Δ of the d-states. The models where also thought to be appropriate fore 3d metals, and although this problem is more complicated due to the d-d interactions, for s-d hybridization the models are appropriate starting points in band structure calculations. It also turned out, that the s-d model can be derived from the Anderson model when U is much larger than Δ .

A milestone of the development was Kondo's observation, that a third order calculation of the resistivity in the s-d model can account for the resistance minimum. In this calculation a term $\log (kT/D)$ appears in third order, D is the free electron bandwidth the next correction is of the order of $J\rho_0(E_F)\log(kT/D)$ and it diverges at $T=0$. This so called Kondo effect placed this problem to the focus of solid state physics for a few years after 1964. Abrikosov and Suhl have demonstrated, that the logarithmic terms are the consequence of a many-body resonance appearing at the Fermi level and subsequent theoretical papers tried to determine the properties of this resonance; the

main goal was to achieve a good quantitative agreement between theory and experiment.

A new line of approach dates back to these years this is called the localized spin fluctuation theory. According to this theory the apprearance of the magnetic moment is the consequence of fluctuations at the impurity site, this model which was supposed to work for nearly magnetic impurities, can also lead to anomalous transport, thermal and magnetic properties, and was in good agreement with the experimental observations on certain alloys.

In parallel to the theoretical development more and more alloys were demonstrated to have anomalous properties, they were interpreted sometimes as Kondo, sometimes as localized spin fluctuation effects. The previous classification of alloy systems which was based an the Hartree-Fock approximation has been extended, the notation of Kondo - or LSF alloys derived from this period. The overall confusion was enhanced by the fact, that the experimental results were heavily influenced by impurity interactions, and a nearly perfect agreement between theory and experiment was merely an antifact than a real progress. The theoretical and experimental state of affairs up to this point are reviewed by Kondo (1969) and Heeger (1969), and later on by Fischer (197o, 1971a).

After 1969 the experimental development is characterized by very careful macroscopie experiments, which have separated the effect of single impurities from spurious anomalies, resulting in a completely different overall picture than that appeared in 1969; this has forced the reexamination of the theory. This renewal, however, was also initiated by the expectation, that a final solution of this particular problem has a much broader aspect, and may be rather useful in other branches of physics, like cathalysis, chemisorption, etc.

Is was realized that the main shortcoming of the classical "solutions" lies in the fact, that only one electron-hole intermediate state is considered in the approximations, this has required an approach to the problem based on a new physical concept. It was first used in other fields of solid state physics, like X-ray absorption where the response of an electron gas to a sudden change in a well localized potential was investigated. The effect is an example of the so called infrared divergency; a spin rotation is a typical case of this effect. The approach - in which an infinite number of electron-hole excitations are considered in the intermediate state - leads to scaling laws with the characteristic feature that the high temperature logarithmic behaviours change to simple power laws at low temperatures. It seems, that this approach has

cleared up the basic physics behind the s-d model, in spite of it still does not predict definite formulas which should match the experimental findings.

The experimental situation appears to be clear again, (the main feature is that no real difference appears between various alloys, and any kind of distinction is artificial) , and complete enough to build up a phenomenological picture which absorbs all the main experimental features, a such kind of model serves as the back bone of this review.

The discussion differs from what is expected from a review which should serve as a guideline for basic understanding the dilute alloy problem. The accuse is our belief, that in this particular field of solid state physics theory and experiment is strongly correlated, and extensive mathematical calculations of simple models are still expected to have their echoes in experimentally determined behaviours.

We start with a short discussion of the basic microscopic models and the relation between them. The structure of the Anderson model will be discussed in more detail in Chapter 3, where the Hartre-Fock approximation and correlation effects in different limits will be examined. Chapter 4 is devoted to the s-d model, and we review the perturbational treatments of the Kondo effect, the one particle intermediate state approximations and the variational treatments of the singlet ground state. The connection between the Anderson

and s-d model will also be discussed in this Chapter. Then we review the main features of the experiments and contrast the results of various macroscopic and local methods with the theoretical situation, the structure of the discussion closely follows the arrangement of the previous Chapters. This shall bring us to the sill unresolved basic questions in the field of dilute alloys, and Chapter 6 is then devoted to the discussion of the latest development of the theory which aims to solve these questions in principle without attempting to account for experimental details.

It would be impossible to give a full list of works which contributed to this field. We have selected those papers which we believe are the most instructive and contain an extensive list of publication on the particular subject.

The reference list of the chapter on the experimental situation is far from being complete, for the reader who is interested in the details we refer to the review papers of Rizzuto 1974 and Grüner 1974.

2. BASIC MODELS

In order to account for physical phenomena caused by a transition metal impurity in nonmagnetic, metallic host one should start with the electronic structure of the impurity atom and describe the interaction of this impurity with the host. In other words, one should find a basic set of wave functions for the collective conduction electron states and for the localized magnetic orbitals, and afterwards to describe the interaction between them (this interaction is called the s-d hybridization). This procedure is analogous to the band structure calculations of transition metals, where one starts with d-electron and conduction electron wave functions. To account for dynamical processes it is however, not necessary to perform a complete "ab initio" calculation of the electronic structure, but merely to find good and simple models which show realistic dynamical behaviours. In the following we briefly describe the different basic models applied to this problem:

(i) Friedel's virtual bound state model (Friedel, 1956, 1958).

(ii) the Anderson model (Anderson, 1961).

(iii) the Wolff model (Wolff, 1961).

2.1 Virtual bound state model.

Friedel (1958) has represented the impurity by a potential. For a given total momentum quantum number ℓ the potential consists of a deep hole at the core of the impurity, and of a centrifugal potential barrier $\ell(\ell+1)/r^2$, where the distance r is measured from the center of the impurity (see figure 1.) .

In this potential hole a bound or resonance state can be formed. Here we deal with resonances, which are near to the Fermi level thus are only partially occupied be electrons rather than with deeply lying bound states which are full. If the resonance levels corresponding to the different spin directions are non-degenerate, a magnetic moment is formed at the impurity site. Considering a transition metal impurity of d- or f-type the resonance is characterized by quantum number $\ell=2$ and $\ell=3$, respectively, later on however, we confine ourselves to $3d$-transition metal impurities.The resonance level has a finite width because the electron may jump from the potential hole to the metallic host by tunnelling through the centrifugal barrier. As the barrier increases with increasing ℓ , relatively narrow levels are expected for $\ell>2$. Friedel has suggested a very elegant description of the resonance formation in

terms of scattering theory. According to this the conduction electrons undergo a resonance scattering due to the processes in which the intermediate state is the resonance state. This resonance scattering can be characterized by an energy dependent phase shift $\delta_{\ell,\sigma}(E)$ and the intermediate state by its density of states $\rho_{\ell,\sigma}(E)$, where σ denotes the spin index. These quanties are given by the form well known in scattering theory, as

$$\rho_{\ell,\sigma}(E) = \frac{1}{\pi} \frac{\Delta}{(E - E_{\ell,\sigma})^2 + \Delta^2} \qquad (2.1)$$

and

$$\operatorname{tang} \delta_{\ell,\sigma}(E) = \frac{\Delta}{E_{\ell,\sigma} - E}, \qquad (2.2)$$

where Δ is the width and $E_{\ell,\sigma}$ the position of the resonance with spin direction σ. Many of the physical quantities can be expressed by the phase shifts, which can be treated phenomenologically, these results will be summerized in chapters 3 and 4.

2.1 Anderson model

Anderson (1961) has suggested a simple model, which is based on Friedel's arguments, but allows direct calculations. In this model the metallic host is represented by electron bands with Bloch states (in the following only one band is retained) with energy ε_k for momentum k . The resonant states discussed by Friedel are treated as extra orbitals; in the most simple idealistic case one orbital with two spin direction $\sigma = +, -$ and energy ε_d is considered. (The energies ε_k and ε_d are measured from the Fermi level.) The transition between this orbital and the conduction electron states with momentum k is represented by an extra term in the Hamiltonian, where the transition amplitude V_{kd} is introduced phenomenologically. Furthermore, Anderson has introduced an intraatomic Coulomb repulsion between two electrons at the localized level to reduce the probability of double occupation. This term plays an important role in the formation of a magnetic moment on the localized orbital and thereby in the magnetic properties of the impurity as in order to be "magnetic" this orbital must be singly occupied. Collecting all the terms, the Anderson Hamiltonian is written in the following form

$$H = \sum_{k,\sigma} \varepsilon_k \, a^{+}_{k\sigma} \, a_{k\sigma} + \sum_{\sigma} \varepsilon_d \, a^{+}_{d\sigma} \, a_{d\sigma} + \qquad 2.3$$

$$+ \sum_{k,\sigma} \left(V_{kd} \, a^{+}_{k\sigma} \, a_{d\sigma} + c.c \right) + U \, n_{d\sigma} \, n_{d-\sigma} \; ,$$

where $a^{+}_{k\sigma}$ and $a^{+}_{d\sigma}$ denote the creation operators of the conduction electrons and the localized d-electrons respectively with spin σ , furthermore, $n_{d\sigma} = a^{+}_{d\sigma} \, a_{d\sigma}$ is the occupation number of the localized level, U is the interatomic Coulomb interaction.

The mixing term has a strong resamblance to that used in band structure calculations where the transition between the d -orbitals and the conduction band is treated by introducing mixing matrix elements, (Heine 1967) . In the present case, the electron may stay on the localized level for finite time only, because ~~it can~~ due to the mixing it will, sooner or later go into the conduction band, thus this mixing term determines the width Δ of the resonance via the "golden rule" as

$$\Delta = \pi \, V^2 \, \rho_0 (\varepsilon_d) \; , \qquad (2.4)$$

where V^2 denotes an appropriate average of $|V_{kd}|^2$ and $\rho_0 (\varepsilon_d)$ stands for the density of states of the conduction electrons in the host metal at the energy of the resonance level. Using this width given by equation (2.4) the density of states of the localized level can be

obtained from equation (2.1) .

The Anderson model in its original form given by equation (2.3) does not describe the orbital degeneracy of the d -level, therefore it has been generalized in several steps. The most general form of the Hamiltonian is as follows

$$H = \sum_{k,\sigma} \varepsilon_k a^+_{k\sigma} a_{k\sigma} + \sum_{\sigma,m} \varepsilon_d n_{m\sigma} + \sum_{k,m,\sigma} (V_{km} a^+_{k\sigma} a_{m\sigma} + c.c)$$
$$+ \frac{U}{2} \sum_{m,m'} n_{m\sigma} n_{m'-\sigma} + \frac{U-\mathcal{J}}{2} \sum_{m\neq m',\sigma} n_{m\sigma} n_{m'\sigma} \qquad (2.5)$$
$$- \frac{1}{2}\mathcal{J} \sum_{m\neq m',\sigma} a^+_{m\sigma} a_{m-\sigma} a^+_{m'-\sigma} a_{m'\sigma} + \frac{1}{2}\mathcal{J} \sum_{m,\sigma} n_{m\sigma} n_{m-\sigma} + (\text{crystal field}),$$

where the index m labels the different d -orbitals, $\mathcal{J}$ is the intraatomic exchange integral between two different orbitals. The "crystal field" terms responsible for the crystalline splitting caused by the non-spherical symmetric crystalline surroundings are not given explicitly, because for d -electrons they probably can be neglected.[x] In the second and third term in the right hand side of

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x
Note
This is not necessarily the case for f -electrons, where the crystalline splitting has a larger effect, because of the very narrow resonances.

equation (2.6) the degeneracy has been taken into account by extending the summation to the different orbitals. The fourth term describes the Coulomb repulsion between two arbitrary electrons with opposite spin. Similarly, the fifth term corresponds to the Coulomb interaction between electrons of parallel spin on different orbitals, and it is completed by the intraatomic exchange interaction. The next terms do not occur in the original paper of Anderson (1961) . As it has been recognized later by Caroli, Caroli and Fredkin (1969), the previous terms are not invariant under a rotation in spin space and in order to restore this symmetry they added the next term. Finally, in a similar way, Dworin and Narath (197o) noticed that the Hamiltonian is still not invariant under a rotation in coordinate space and they completed it by the last term.

As it will be discussed later on several of the results are modified compared with the nondegenerate model in such a simple way that formally J is replaced by $U+4J$ in the final formulae. The quantity $U+4J$ can be considered as an effective Coulomb integral and later where it does not lead to misunderstanding it will be simply referred to as Coulomb integral.

The essential feature of the Anderson model is that by introducing extra orbitals one arrives at a dynamical model which fits Friedel's picture perfectly well as far as the

the formation of the virtual bound is state concerned. Conceptionally, however there is a serious difficulty, namely the translationally invariant conduction electron wave functions form a complete set, thus the extra orbitals are not orthogonal to this set. Similar orthogonalization problems appear in the different band structure calculations for normal and more seriously for transition metals (Heine 1967) . However, in the present case this non-orthogonality is not expected to influence essentially the dynamical properties, but they might rather show up in comparison with ab initio calculations. As the Anderson model us usually used to investigate the dynamical behaviour of the impurity, this orthogonality problem is rather academic in that context.

2.3 Wolff model.

Another simple model has been constructed by Wolff (1961). The electronic states are restricted to a single band described in terms of Wannier functions localized at atomic sites. The impurity potential is represented by the Wannier function centered at the impurity site i . The width of the energy band is determined by the hopping matrix elements T_{ij} between Wannier functions centered at site i and j . The matrix elements connecting the impurity orbital to the host states, are different from the hopping matrix

element between the host atoms. Finally, similarly to the Anderson model, a Coulomb repulsion U is introduced which acts between two electrons with opposite spins at the impurity. The Hamiltonian is given as

$$H = \sum_{i \neq j, \sigma} T_{ij} d_{i\sigma}^{+} d_{j\sigma} + \frac{U}{2} \sum_{\sigma} n_{o\sigma} n_{o-\sigma} + V \sum_{\sigma} n_{o\sigma} \quad (2.7)$$

where $d_{i\sigma}^{+}$ is the creation operator of an electron with spin σ and orbital centered at site i and $n_{o\sigma} = d_{o\sigma}^{+} d_{o\sigma}$ where the impurity site is labeled by o .

This model has strong resamblance to the Anderson model discussed before, which is obvious if in the Anderson model the conduction electron wave functions are transformed to Wannier representation (Rivier and Zitkova 197o) involving all of the conduction bands, though, in the Wolff model only one band is considered.

The most attractive feature of the Wolff model is that no extra orbital has been introduced for the impurity. Other serious conceptional problems must be raised, however e.g. that the impurity orbital is not well localized as it is represented by a Wannier function, contrary to the Anderson model, where the localized orbital is constructed using several bands.

The dynamics in the Wolff model shows a behaviour similar to that found for Anderson model which will be discussed along this paper (see e.g. Appelbaum and Penn 1969, 1971), however there are essential differences as well (see e.g. Fischer 1971b). The differences can be domonstrated on the following example of the electrical resistivity. In the Anderson model if the transition rate from the conduction band to the impurity level, V_{kd} tends to zero a free electron band is obtained which is not coupled to the impurity level and the impurity resistivity is vanishing. In the Wolff model, however, taking the hopping matrix elements T_{io} and T_{oi} which connects the impurity level to the other electrons to be zero, a large impurity resistivity most be expected, because the conduction electrons should go around the impurity atoms [illegible]. In this sense, a careful analysis of the applicability of the Wolff model is needed, which may result in a better understanding of the theories obtained in this model (e.g. Kaiser and Doniach 1970).

2.4 Estimations of the basic parameters of the Friedel and Anderson models.

In order to estimate the width Δ , Anderson and McMillan (1967) performed an "ab initio" calculation starting with the "muffin-tin" idea (see e.g. Ziman 1972) worked out for band structure calculations. In this method atomic wave functions are used inside a sphere surrounding the core of the atoms and free electrons outside them. A special matching condition was elaborated in the augmented plane wave (APW) method. Anderson and McMillan adopted this method to the single impurity problem, where atomic wave functions are used inside the muffin-tin sphere of the impurity and free electron wave functions outside. As in the APW method, one determines the phase shifts of the conduction electrons scattered by the atomic core inside the sphere. Such a calculation fits perfectly Friedel's description sketshed briefly in section 2.2. By making use of the Friedel sum rule to be discussed in section 3.5 Anderson and McMillan have determined the extra density of states localized at the impurity site in terms of the energy derivatives of the phase shifts, $\frac{\partial \delta_\ell(E)}{\partial E}$. By calculating these derivatives $\frac{\partial \delta_\ell(E)}{\partial E}$ the additional density of states $\Delta\rho(E)$ produced by the impurity in the free electron gas can be obtained by the formula

$$\Delta\rho(E) = \frac{1}{\pi}\sum_{\ell}(2\ell+1)\frac{\partial\delta_\ell(E)}{\partial E} \quad , \qquad (2.6)$$

where the summation goes over the different angular momenta ℓ and the factor $(2\ell+1)$ is due to orbital degeneracy. The actual calculation has been performed for Fe impurity in Cu and yiels the density of states given in figure 2., in which a pronounced resonance is formed with width of 1-2 eV. This value of the width allows us to determine the average value of the mixing amplitude V_{kd} of the Anderson model by equation (2.4) . The position of the resonance is about lo eV measured from the bottom of the conduction band and therefore the resonance can be found in the neighborhood of the Fermi level. One cannot calculate the Coulomb integral by considering the atomic orbital in a simple way, because the Coulomb interaction is strongly screened by the conduction electron. This screening may reduce it's value essentially to 1-3 eV (see e.g. Herring 1966) while the integration of atomic wave functions yields about lo eV. Furthermore, using the estimation $\mathcal{J} \sim$ o,5-1 eV we get effective Coulomb integral $U+4\mathcal{J} \sim 5$ eV.

3. BASIC RESULTS IN THE ANDERSON MODEL

All the three models discussed until now are capable to describe the resonance formation due to a transition metal impurity embedded in a metallic host. Since from the physical point of wiew the Anderson model is nearer to the situation we are interested in [redacted] than the Wolff model, and can be treated mathematically more exactly than Friedel's description, in the following we restrict our discussion to the analysis of the Anderson model. It should be pointed out, however, that the dynamical properties of these models are very similar, for example the localized spin fluctuations (LSF) which will be discussed later exhibit similar features in the Anderson and Wolff models (Appelbaum and Penn 1969, 1971).

First let us discuss two limiting cases of the Anderson model. In one limit the broadening of the localized level can be neglected compared to the Coulomb interaction, i.e. $\Delta \ll |\varepsilon_d|$ and $\Delta \ll U$. If the impurity level is below the Fermi level $(\varepsilon_d < 0)$ it is at least single occupied in thermal equilibrium. Assuming that there are two electrons on the impurity level the total energy due to the Coulomb repulsion becomes $2\varepsilon_d + U$. If $2\varepsilon_d + U < 0$ the level is doubly occupied and the magnetic moments of the two electrons localized on the impurity compensate each

other thus the impurity is non-magnetic. If on the other hand, $2\varepsilon_d + U > 0$ then the impurity is singly occupied and a magnetic moment is formed with spin $\pm$ 1/2. We will be interested mainly in the latter case where the impurity can be magnetic.

The other limit of considerable interest is, the situation when a broad resonance level is formed at the Fermi level and the Coulomb energy is relatively small compared to the width of this level, i.e. $|\varepsilon_d|, U \ll \Delta$. In this case, the Coulomb energy U being small can not modify essentially the density of states related to the localized level. Thus the impurity is partially occupied with spin up and spin down electrons. This state is obviously non-magnetic, only the fluctuation in the occupation numbers for different spins can result in magnetic moment formed temporarily for a short time. This phenomenon is known as localized spin fluctuation, LSF.

Changing the relative value of the parameters Δ, U and ε_d between these two limiting cases the magnetic limit goes over continuously to the nonmagnetic one. The Hartree-Fock HF approximation (Anderson 1961) leads to a sharp transition between the magnetic and non-magnetic cases since it corresponds to the approximation of a static mean-field theory neglecting fluctuations.

In the present chapter after referring to some general features of the theory we are going to discuss

(i) the Hartree-Fock approximation,

(ii) the localized spin fluctuation considering electron-hole and electron-electron correlation,

(iii) the perturbational treatment of the Anderson model in the large U/Δ limit, and finally

(iv) we list a series of arguments valid generally in the Anderson model.

3.1 General structure of the Anderson model.

The Hamiltonian can be given by equation (2.3) in the simplest case with only one localized orbital where there are two different interaction terms, the s-d mixing characterized by the transition rate V_{kd} and the intraatomic Coulomb repulsion U . As the first of these interactions is quadratic in the operators, neglecting the Coulomb repulsion U the Hamiltonian can be diagonalized exactly. In the case $U=0$ the conduction electrons can be eliminated by introducing a broadening for the localized level. This broadening can be given by

$$\Delta = \pi \overline{|V_{kd}|^2} \rho_0 (E_{d,\sigma}) \quad , \tag{3.1}$$

where the bar over $|V_{kd}|^2$ means an average over the directions of k. Thus Δ is proportional to the density of states of the conduction electrons at $E_{d,\sigma}$, which in turn may depend on the spin direction and will be determined later. Usually $\rho_o(E_{d,\sigma})$ is replaced by the density ρ_o, taken at E_F. In this way ~~at zero temperature one may write~~ the one-particle Green's function for the extra orbital can be written at zero temperature as

$$G^{(o)}_{d,\sigma}(\omega+i\varepsilon) = \frac{1}{\omega - E_{d,\sigma} + i\Delta}, \quad \varepsilon \to +0 \tag{3.2}$$

where the index o reflects the fact that the Coulomb interaction has not been taken into account except for the fact, that the position of the resonance $E_{d,\sigma}$ depends on U. The density of states of this single orbital, which can be obtained from the Green's function of equation (3.2) as

$$\rho^{(o)}_{d,\sigma}(\omega) = -\frac{1}{\pi} \operatorname{Im} G^{(o)}_{d,\sigma}(\omega+i\varepsilon) = \frac{1}{\pi} \frac{\Delta}{(\omega - E_{d,\sigma})^2 + \Delta^2} \tag{3.3}$$

has a simple Lorentzian form for $U=o$. By comparing this formula with equation (2.1), the connection between the Friedel's resonance theory and the Anderson model can be demonstrated. It is important to note that this density of states is normalized to unity, this normalization is not changed by including the effect of the Coulomb interaction, i.e.

$$\int \rho^{(0)}_{d,\sigma}(\omega)\, d\omega = \int \rho_{d,\sigma}(\omega)\, d\omega = 1 \qquad (3.4)$$

The impurity Green's function, and in particular its spectral function the density of d-states $\rho_{d,\sigma}(\omega)$ is of primary importance, as the various physical parameters are determined by this quantity.

First of all, we will consider that part of the one electron scattering amplitude in which only one electron is in the scattered state and the spin is not changed during the scattering process. As the conduction electrons are directly involved only in the mixing interaction, considering an arbitrary one-electron scattering process the first interaction is a transition of the conduction electron to the localized level and the last one is the reverse process. All the processes in between can be related to the behaviour of the broadened localized level, which can be described by the localized level Green's function $G_{d,\sigma}(\omega)$ renormalized by the Coulomb repulsion.

Thus

$$t_{kk',\sigma}(\omega) = V_{kd}\, G_{d,\sigma}(\omega)\, V_{dk'} \qquad (3.5)$$

where $t_{kk',\sigma}(\omega)$ is the non-spin-flip scattering amplitude of the conduction electrons with incoming and outgoing

momenta k and k'.

Taking the imaginary part of equation (3.3) one obtains

$$\mathrm{Im}\, t_{kk,\sigma}(\omega) = \pi |V_{kd}|^2 \rho_{d,\sigma}(\omega) \qquad (3.6)$$

i.e. $\mathrm{Im}\, t_{kk,\sigma}(\omega)$ is entirely determined by the density of states of the d-level.

This equation plays a central role in the dilute alloy problem because according to the "optical theorem" the total scattering cross section is proportional to the imaginary part of the forward scattering amplitude $t_{kk,\sigma}(\omega)$ and therefore it is proportional to $\rho_{d,\sigma}(\omega)$.

This connection is the reason of the many theoretical attempts which have been made to calculate the renormalized density of states of one localized level. This renormalization in spite of the apparent simplicity of the corresponding term $U n_\sigma n_{-\sigma}$ in the model, is still missing for finite Coulomb interaction and no reasonable approximation is known yet which works for arbitrary Coulomb energies. The approach as outlined above treats first the mixing between the d- and conduction electron states, and then includes the effect of the Coulomb interaction, thus clearly this procedure should be more appropriate for small U values.

Finally it should be mentioned that if we were to consider the more realistic case where the d-level is fivefold degenerate and the Hamiltonian is given by equation (2.3) then we should take into account the symmetry of d-level ($\ell=2$). Due to this symmetry the product $V_{kd} V_{dk'}$ occuring in many formulae (see e.g. equation 3.5) has an angular dependence

$$V_{kd} V_{dk'} = V^2 P_\ell (\cos \gamma_{kk'}) = V^2 (2\ell+1) \sum_{m=-\ell}^{\ell} Y_\ell^{m*}(k) Y_\ell^{m}(k') , \quad (3.7)$$

where Y_ℓ^m is the spherical harmonics, P_ℓ is the Legendre polynomial, $\gamma_{kk'}$ is the angle between momenta k and k', and V is the transition amplitude. Furthermore, according to equations (3.5) and (3.7) the scattering amplitude can be given in the following form

$$t_{kk'}(\omega) = t_{\ell=2}(\omega) P_{\ell=2}(\cos \gamma_{kk'}) , \quad (3.8)$$

where $t_\ell(\omega)$ denotes the partial scattering amplitude for angular momentum ℓ.

3.2 Hartree-Fock treatment of the Anderson model

In the Hartree-Fock approximation (Anderson 1961) the effect of the Coulomb interaction is taken into account by an "effective field" which results in energy shifts $E_{d,\sigma} - \varepsilon_d$ but does not alter the shape (Lorentzian for $U=0$) of the levels. These shifts should be determined in a self-consistent way allowing for different occupation of the levels.

Let us restrict our treatment to the most simple case given by equation (2.4) with two levels $\sigma = \pm 1$.
The occupation numbers are expressed as

$$\langle n_{d\sigma} \rangle = \int_{-\infty}^{0} \rho_{d,\sigma}^{(\omega)}(\omega)\, d\omega = \frac{1}{\pi} \cot^{-1}\left(\frac{E_{d,\sigma}}{\Delta}\right), \quad (3.9)$$

where the energy (ω) is measured form the Fermi energy and equation (3.3) has been applied. The averaged Coulomb field acting on the level σ is $U\langle n_{d-\sigma}\rangle$, thus

$$E_{d,\sigma} = \varepsilon_d + U\langle n_{d-\sigma}\rangle \quad . \quad (3.10)$$

Inserting these results into equation (3.9) two coupled equations are obtained

$$\langle n_{d+} \rangle = \frac{1}{\pi} \cot^{-1}\left(\frac{\varepsilon_d + U\langle n_{d-}\rangle}{\Delta}\right) \quad (3.11)$$

and

$$\langle n_{d-} \rangle = \frac{1}{\pi} \cot^{-1}\left(\frac{\varepsilon_d + U\langle n_{d+}\rangle}{\Delta}\right).$$

Depending on the relative values of the different parameters ε_d, U, Δ this system of equations may have a single solution, with $\langle n_{d+}\rangle = \langle n_{d-}\rangle$ in which case the impurity is non-magnetic, or (in addition) two symmetrical solutions with $\langle n_{d+}\rangle \neq \langle n_{d-}\rangle$ and then the impurity is magnetic. For U=0 the trivial solution $E_{d,\sigma} = \varepsilon_d$ corresponds to a non-magnetic state. Increasing the value U the impurity remains non-magnetic and at a critical value of U it becomes magnetic. Equation (3.11) can be solved by graphical method plotting $\langle n_{d+}\rangle$ against $\langle n_{d-}\rangle$ using the first equation and vica

versa, the crossing points of these curves yield the solutions. Two typical diagram is given in figure 3/a using parameter values $U/\Delta = 5$, $\varepsilon_d = -U/2$ and $U/\Delta = 1$, $\varepsilon_d = -U/2$ respectively. The magnetic and non-magnetic regions of the parameters are plotted in figure 3/b.

The boundary line separating the magnetic and non-magnetic regions can be derived in a simple way. Let us suppose that the occupation number at a given point of the boundary is n_c. By increasing U one may get a solution in the form $\langle n_{d+} \rangle = n_c + \delta n$, $\langle n_{d-} \rangle = n_c - \delta n$. This solution must satisfy equation (3.11) in this point with infinitisimal small δn thus n_c must be a solution of the derivative of equation (3.7)

$$1 = \frac{U}{\pi\Delta} \frac{1}{1 + \left(\frac{\varepsilon_d + U n_c}{\Delta}\right)^2} \qquad (3.12)$$

This result can be rewritten by using equation (3.3) as

$$U \rho_d^{(o)}(0) = 1 \qquad 3.13$$

and shows that a system is more likely magnetic if the density of d-states is large at the Fermi level. Thus the most favorite case for formation a magnetic moment is that where the impurity levels of Lorentzian shape are half filled by electrons (e.g. as we shall see later Mn in Cu). Furthermore, if the impurity levels are nearly empty or almost completely full then the impurity is more likely

non-magnetic as $\rho^{(0)}_{d,\sigma}(0)$ is relatively small. This condition can be obtained immediately by considering the balance of the "kinetic energy" increase and the interaction energy gain near the boundary. Since due to a polarization $\langle n_{d\pm} \rangle = n_c \pm \delta n$ the kinetic energy increases by $\rho_d^{(0)}(0)^{-1}(\delta n)^2$ this condition has the form

$$\rho_d^{(0)}(0)^{-1}(\delta n)^2 + U\left[(n_c-\delta n)(n_c+\delta n) - n_c^2\right]$$

which is equivalent to equation (3.13) . The relation derived here has the same form as the Stoner condition obtained for the magnetic instability of an electron gas (Stoner 1938 , 1939).

Similar consideration can be applied to the fivefold degenerate case $l=2$ as well where the levels are labeled by quantum numbers m=-2, -1, o, 1, 2. In this case, however, there might be two different kinds of magnetism, spin and orbital one. For spin magnetism the different levels are equally polarized and thus near the boundary $\langle n_{d\,m\pm} \rangle = n_c \pm \delta n$ for arbitrary m . By repeating our previous reasoning for the Hamiltonian given by equation (2.5) one finds that the last two terms of the Hamiltonian do not contribute to the HF energy, because they are off-diagonal, thus the condition of spin magnetism is

$$(U + 4J)\rho_d^{(0)}(0) > 1 \qquad (3.14)$$

For the investigation of orbital magnetism we take as a sipmle example an impurity with twofold orbital degeneracy.

Orbital magnetism appears if the populations of the two orbitals are different, but this difference is spin independent. Denoting the orbitals by 1 and 2, $\delta n_{1\sigma} = -\delta n_{2\sigma'}$ for arbitrary σ and σ'. The condition necessary for orbital magnetism can be obtained in a simple way, as

$$(U - J)\rho_d^{(0)}(0) > 1 \qquad (3.15)$$

As the exchange integral J is positive one can immediately see by comparing equations (3.14) and (3.15) that the occurance of spin magnetism is more favourable than that of orbital magnetism, furthermore, spin magnetism is more likely for a degenerate orbital than for a nondegenerate one.

In HF approximation several quantities can be expressed in terms of phase shifts which are the key quantities in Friedel's theory. The requirement that the conduction electron scattering amplitude can be expressed by phase shift in an angular momentum channel ℓ is that the scattering be elastic and only the one excitation channel without spin-flip be effective. This is an extremely strong condition, it is, however, satisfied in HF approximation because the dynamical effects are excluded. The phase shift is related to the scattering amplitude as

$$t_{\ell,\sigma}(\omega) = \frac{1}{\pi\rho_0} \sin\delta_{\ell,\sigma}(\omega)\, e^{i\delta_{\ell,\sigma}(\omega)} \qquad (3.16)$$

where $t_{\ell,\sigma}(\omega)$ is defined by equation (3.8). The phase shifts depend on energy and in the magnetic case on σ as well. By considering equations (3.16), (3.8), (3.3) and (3.1) the phase shift can be expressed as

$$\delta_\sigma(\omega) = \cot^{-1}\left(\frac{E_{d,\sigma}}{\Delta}\right) = \cot^{-1}\left(\frac{\varepsilon_d + U\langle n_{d-\sigma}\rangle}{\Delta}\right) = \pi\langle n_\sigma\rangle, \tag{3.17}$$

where the last equality follows from equation (3.9). It is special case of the Friedel sum rule (see e.g. Ziman 1973) which relates the phase shifts to the number of electrons screening the excess charge of the impurity. In the present case, the Friedel sum rule is satisfied by considering only the electrons on the impurity level.

The ionic charge Z of the impurity ion measured in electronic unit, must be screened by the electrons on the impurity level and by the conduction electrons. However, according to our previous result the conduction electrons do not contribute to the Friedel sum rule, therefore, the screening is entirely due to the electrons on the impurity level. Thus, the condition of screening is

$$Z = 5\left(\langle n_{d\sigma}\rangle + \langle n_{d-\sigma}\rangle\right) = \frac{5}{\pi}\left(\delta_\sigma + \delta_{-\sigma}\right), \tag{3.18}$$

where the orbital degeneracy is responsible for the factor of five and equation (3.9) has been applied.

The condition of screening occurs in the mathematical schema in the following way. In the Anerson model the quantities V_{kd}, U and J can be obtained at least in principle by calculating the electronic structure of the impurity and they are more or less independent of the particular 3d-impurity in the same host. In contrary to these quantities the position of the d-level ε_d strongly depends on the occupation of the d-level, thus on the charge of the impurity ion. The impurity ion produces a strong Coulomb field which shifts the value of ε_d in such way that the ion is completely screened at the impurity site. This screening can be formulated as a self-consistant condition to determine the position of the d-level ε_d.

Let us turn to the discussion of the magnetic polarization of the impurity. The magnetic moment of d-electrons can be expressed in a way similar to (3.18) by the number of d-electrons.

$$M = \mu_B \sum_{m=-\ell}^{\ell} \left(\langle n_{dm+} \rangle - \langle n_{dm-} \rangle \right) = 5\mu_B (\delta_+ - \delta_-) \quad , \tag{3.19}$$

where μ_B is the Bohr magneton. Thus, in HF approximation the magnetic moment localized on the d-level is proportional to the difference of the phase shifts. Furthermore, it is important to point out that the conduction electrons are not essentially polarized as it has been shown by Anderson (1961). Thus, the s-d mixing term may lead to a polarization of the conduction electrons which is parallel to that of the d-electrons, because the polarized d-electrons can jump to the conduction band and vica versa, this effect is, however, compensated by the energy shift of the conduction electrons caused by the presence of the resonance (Anderson's "compensation theorem"). In other words, the conduction electron-impurity scattering does not change the total conduction electron density of states in the region of the Fermi level, provided the scattering is independent of the momenta of the conduction electrons and the band is symmetric to the Fermi level. The fact that these assuptions are fulfilled approximatly only does not change the compensation drastically. Thus, in the HF approximation the magnetic moment is completely localized on the d-level.

The magnetic susceptibility can be calculated by using the expression (3.19) and one arrives at a Curie-like temperature dependence M^2/T . This result may be modified going beyond the HF approximation, however, a clear distinction between magnetic and non-magnetic limit can be made on the basis of the HF approximation.

The density of states of the d-level is entirely different in the non-magnetic and magnetic limit. In the non-magnetic limit a simple Lorentzian density of states is obtained which is filled in by electrons to the same energy for both spin directions. In the magnetic limit, however, according to equation (3.1o) the positions of the two Lorentzian levels are different and

$$E_{d,\sigma} - E_{d,-\sigma} = U\left(\langle n_{-\sigma}\rangle - \langle n_{\sigma}\rangle\right) . \qquad (3.2o)$$

The density of states for different spin directions is shown in figure 4., where the occupied regions are shaded in different ways for spin up and spin down electrons, the total density of states

$$\rho_{d,total}(\omega) = \rho_{d,\sigma}(\omega) + \rho_{d,-\sigma}(\omega) \qquad (3.21)$$

is represented by the dotted line. The separation between these peaks is proportional to the Coulomb energy and to the magnetization, see equations (3.2o) and (3.19) .

At zero temperature the impurity resistivity R is proportional to $\rho_{d,total}(0)$ since the cross section for the conduction electrons is expressed by the forward scattering amplitude (optical theorem) which in turn is given by equation (3.6). Summing over the spin directions ~~in the HF approximation~~ the electrical resistivity has the form

$$R(T=0) = \frac{1}{4\pi k_F e} \operatorname{Im}\left(t_{kk,\sigma}(\omega=0) + t_{kk,-\sigma}(\omega=0)\right) = \tag{3.22}$$

$$= \frac{1}{4\pi k_F e} |V_{kd}|^2 \rho_{d,total}(\omega=0)$$

where k_F is the Fermi momentum and e is the electronic charge.

Applying this formula to interpret the experiments the electrical resistivity can be used to obtain information on the structure of the d-level. One can distinguish between non-magnetic and magnetic cases by measuring the resistivity as a function of the atomic number of the impurities (Friedel 1958) . Similar situation can be expected for the amplitude of the charge polarization around an impurity and this effect will be discussed in chapter 5.

It is very important to emphasize that these considerations are valid only in the HF approximation. At low temperature strong correlations in the neighbourhood of the Fermi energy might give rise to an essential modification of the HF results.

As it will be shown later these correlations might be suppressed by increasing the temperature, thus one may expect that the HF situation is a good approximation at high temperatures where the different quantities depend only slightly on temperature, as kT is always negligible compared to U and Δ . Therefore Friedel's argument on the resistivity holds only in the high temperature region and at low temperatures intensive many body effects can be expected.

In the following we speak about magnetic or non-magnetic impurities depending on whether the total density of states is well split or non-split, the relation of this behaviour to the magnetic properties has been shown before. The case, where there is only a relatively small splitting, will be referred to as intermediate case. The aim of the next section is to study the effect of correlations in the limit where $U \ll \Delta$; the magnetic limit will be the subject of chapter 4.

3.3 Correlation effects in the non-magnetic limit

In the non-magnetic limit the position of the resonances and the occupation numbers are independent of the spin direction σ . The results of the HF approximation are not different from the $U=0$ limit, except that the position of the resonance level is shifted by $U\langle n_\sigma \rangle$. Correlation effects

due to the Coulomb repulsion appear only beyond the HF approximation. Two types of correlations may occur considering the localized level: electron-electron with total spin $S=0$ and electron-hole with spin $S=1$. In diagrammatic representation these correlations can be characterized in lowest order by the first order vertex corrections containing two parallel or two antiparallel lines, respectively. These diagrams are shown in figure 5., where the solid and dotted lines represent the electrons and the Coulomb interaction, respectively. The strengths of the different correlations depend very much on density of electrons $n=\langle n_\sigma \rangle$, therefore the discussion is split into two parts (i) low density $n \ll 1$ limit (which is equivalent to the high density limit $n \approx 1$ due to electron-hole symmetry), (ii) symmetrical case when $n = 1/2$.

(i) low density limit

As it has been pointed out by Schrieffer and Mattis(1965) in the low density limit the electron-hole correlation can be neglected, because the amplitude of any process in which a hole is involved, is proportional to the probality of creation of a hole thus to the density of electrons which is a small quantity $n \ll 1$. Therefore, the amplitude of any correlation effect, in which electron-hole pairs

are involved, is negligible compared to processes in which two electrons are interacting. In diagrammatic representation only the electron-electron ladder diagrams shown in figure 5/b. are important, According to Schrieffer and Mattis(1965) these electron-electron correlations can be taken into account by introducing an effective Coulomb interaction, $U_{eff}^{(e-e)}$ which is the sum of a geometric series corresponding to successive electron-electron scatterings. For zero frequency this interaction has the following form

$$U_{eff}^{(e-e)} = \frac{U}{1 + \frac{U}{\pi \Delta} \tan^{-1}\left(\frac{\varepsilon_d}{\Delta}\right)} \qquad (3.23)$$

where $\varepsilon_d < \Delta$. Furthermore, the condition for the formation of magnetic moment is

$$U_{eff}^{(e-e)} \rho_d^{(o)}(0) > 1 \qquad (3.24)$$

which is similar to the condition obtained in HF approximation (see equation 3.13) but U is replaced by $U_{eff}^{(e-e)}$.

Inserting the expression of $\rho_d^{(o)}(0)$ given by equation (3.3) it is easy to see that this condition is never satisfied. Therefore Schrieffer and Mattis concluded that at least in the low density limit the correlations are of extreme importance, as the fluctuations can prevent the system from a transition to the magnetic limit. For degenerate d-levels

however they have found that although the condition for magnetic transition is weaker than in HF approximation, the formation a of magnetic moment is still possible, because the exchange interaction tends to align the spins.

(ii) symmetrical case

In this case the position of the localized impurity level is symmetric with respect to the Fermi level i.e. $E_{d,\sigma} = \varepsilon_d + \frac{U}{2} = 0$. The problem in this case is more difficult than the previous limit, because both channels are of equal importance. In spite of this a large number of theoretical works are based on the supposition that the dominant correlation is the electron-hole one as the formation of magnetic moment is the result of this correlation effect. A detailed analysis of these theories is given by Mills, Beal Monod and Lederer (1973), the present discussion will be restricted only to the main ideas.

The dominance of the electron-hole correlation has been first suggested probably by Suhl (1967) and many details have been worked out by him and his coworkers (Levine and Suhl 1968; More and Suhl 1968; Levine, Ramakrishnan and Weiner 1970). Lederer and Mills (1967) presented a similar theory which closely follows their previous work (Mills and Lederer 1966) on nearly magnetic metals where they call the dominant electron-hole correlation as localized paramagnon. Concerning measurable

quantities the most detailed version of this theory called the localized spin fluctuation (LSF) theory has been presented by Rivier and Zuckerman (1968) and by them and Sunjic (1968) and they have even made an attempt to find equivalence between this problem and the Kondo effect.

The mathematical treatment is similar to the theory of Schrieffer and Mattis (1965) discussed previously, but here successive electron-hole scatterings are considered thus the electron-hole ladder diagram are summed up. Here again, an effective Coulomb interaction $U_{eff}^{(e-h)}$ can be introduced as

$$U_{eff}^{(e-h)} = \frac{U}{1 - U \rho_d^{(0)}(0)} \qquad (3.25)$$

By comparing this formula with equation (3.23) one finds an essential difference namely in the sign appearing in the denominator. This formula describes an enhancement of the interaction and diverges as the HF instability given by equation (3.13) is approached. A further important consequence of this theory is that at low frequencies ω the dynamical susceptibility of the electrons on the d-level $\chi(\omega)$ exhibits a peak which is narrowed due to this enhancement and can be written in the form

$$\chi(\omega) = \frac{1}{\pi} \frac{1}{\omega + i \cdot \tau_0^{-1}} \qquad (3.26)$$

where τ_0 is called the life time of the localized spin fluctuations, It containts the enhancement factor $(1 - U\rho_d^{(\omega)}(0))^{-1}$ as

$$\frac{1}{\tau_0} = \frac{\pi \rho_d^{(0)}(0)}{1 - U \rho_d^{(0)}(0)} \qquad (3.27)$$

The most important consequence of this echancement is the deformation of the density of states $\rho_d^{(0)}(0)$ in such a way that the second derivative of $\rho_d^{(0)}(0)$ taken at $\omega = 0$ is enhanced by the factor $(1 - U\rho_d^{(0)}(0))^{-1}$ furthermore the temperature and energy dependence is similar to that of a Lorentzian resonance. Using equation (3.6) similar results can be derived for the imaginary part of the forward scattering amplitude, as well. At low temperature this behaviour leads to enhanced, T^2-temperature dependence which occurs in several physical quantities. As these predicted temperature dependences and enhancements are in accordance with the experiments the localized spin fluctuation theory is believed by many to be verified experimentally. Although since that time great attempt has been made, to clarify wheather the electron-hole correlations dominate over the electron--electron correlations, unfortunatly, only few papers have been published in this line. Beal-Monod, Hurault and Maki (1970) still preferred the paramagnon propagation, but they have concluded that the ladder approximation is not sufficient. Furthermore, Weiner (1971) made an attempt to treat both channels i.e. electron-electron and electron-hole correlations simultaneously without arriving at a definite condlusion.

Realizing the abovementioned difficulties Iche and Zawadowski (1972) have recently focused their attention to the symmetry properties of the symmetric Anderson model ($\varepsilon_d + \frac{U}{2} = 0$) instead of performing concrete calculations. In this case the Anderson Hamiltonian given by equation (2.3) can be written in the form

$$H = -\frac{U}{4} + H_U$$

where

$$H_U = \sum_{k,\sigma} \varepsilon_k a^+_{k\sigma} a_{k\sigma} + \sum_{k,\sigma} (V_{kd} a^+_{k\sigma} a_{d\sigma} + c.c.) + U (n_{d+} - \tfrac{1}{2})(n_{d-} - \tfrac{1}{2}) \quad . \tag{3.28}$$

It is easy to show that the Hamiltonian H_U exhibits electron-hole symmetry if the conduction electron band is symmetric with respect to the Fermi level. According to Iche and Zawadowski (1972) one can perform an electron-hole transformation for one spin direction without any change in the Hilbert space of the other spin direction and then the Hamiltonian is invariant under this transformation if one changes simultanously the sign of the Coulomb interaction, as well. This means that if repulsion acts between two electrons then the electron-hole interaction is similar but attractive. This symmetry provides us with several identities e.g. $\langle H_u \rangle = \langle H_{-u} \rangle$ thus disregarding the term $-\frac{U}{4}$ the ground state energy is even function

of U as it has been previously shown by Yosida and Yamada (1971) using time dependent Green's functions. Similar result follows for the self-energy. Generally, one can connect the electron-electron and electron-hole correlation function by the exact identity

$$\langle a_{d\sigma}(t)\, a_{d-\sigma}(t)\, a^{+}_{d-\sigma}(t')\, a^{+}_{d\sigma}(t') \rangle_{U} = \tag{3.29}$$

$$= \langle a^{+}_{d\sigma}(t)\, a_{d-\sigma}(t)\, a^{+}_{d-\sigma}(t')\, a_{d\sigma}(t') \rangle_{-U}$$

where the subcripts U and $-U$ refer to the sign of U in the Hamiltonian occuring in the thermodynamical average. This identity obviously shows that the two different correlations have the same amplitude in any order of perturbation theory, there is only a difference in sign in odd orders. As a special case this shows that the two unrenormalized (with respect to U) correlation functions have the same alaytical form. In this way it has been generally proved that a correct theoretical answer can be expected only on the basis of such theory where the electron-electron and electron-electron-hole correlations are treated on an equal footing. The diagrams where the two channels are mixed together are the so called "parquet diagrams", whose calculation seems to be a very difficult task. Finally, it must be mentioned that the symmetry consideration discussed above cannot be generalized to the case of orbital degeneracy with exchange inter-

action.

Recently, the symmetrical Anderson model has been the subject of investigations using scaling idea in two different ways. Hertz (1971) has worked with the functional integral method applied to the Anderson model by Wang, Evenson and Schrieffer (1969) and Iche (1973) has turned to the renormalization group technique. These methods will be discussed in chapter 6., here we refer only to some important results. In the first method the fluctuations of high frequencies, in the second the scattering processes with higher energies have been eliminated by introducing a new, effective coupling constant U_{eff}. Using the renormalization group technique in the first approximation which is equivalent to considering the "parquet diagrams" only it has been found that $U_{eff} = U$ while in the second approximation going just beyond the "parquet diagrams" $U_{eff} \leq U$ has been obtained in agreement with the functional integral method. It is worth to mention that considering only the localized paramagnons by neglecting the electron-electron correlations the renormalization group method reproduces the ~~which is~~ expression of U_{eff} given by equation (3.25) with the enhancement factor $(1 - U\rho_d^{(0)}(0))^{-1}$. In this way, it is shown that the more accurate theories

do not yield an enhancement of this type, thus the localized paramagnon picture with such an enhancement is not realistic at all.

Finally we mention the recent works by Menyhárd (1972, 1973) who has made an attempt to reinvestigate the question of dominant diagrams. She has calculated the ground state energy and the satic susceptibility up to forth and third orders, respectively, using a time ordered diagram technique developed by Yosida and Yamada (1971). The conclusion was that in a given order in U the contribution of all the diagrams is of the same order of magnitude. Furthermore, the ground state energy E_g and the static susceptibility χ were compared with the expressions obtained considering only electron-hole correlations. The results as

$$E_g = -\frac{U}{4} + \left\{ -0.11 \left(\frac{U}{\pi\Delta}\right)^2 + 0.006 \left(\frac{U}{\pi\Delta}\right)^4 + \dots \right\} \Delta \qquad (3.30)$$

and

$$\chi = \frac{\mu_B^2}{2\pi\Delta} \left\{ 1 + \frac{U}{\pi\Delta} + 0.54 \left(\frac{U}{\pi\Delta}\right)^2 + 0.21 \left(\frac{U}{\pi\Delta}\right)^3 + \dots \right\} \qquad (3.31)$$

are in strong-disagreement with those obtained by considering the electron-hole correlations only

$$E_g^{LSF} = -\frac{U}{4} + \left\{ -0.11 \left(\frac{U}{\pi\Delta}\right)^2 - 0.048 \left(\frac{U}{\pi\Delta}\right)^4 \dots \right\} \Delta \qquad (3.32)$$

and

$$\chi^{LSF} = \frac{\mu_B^2}{2\pi\Delta} \frac{1}{1-\left(\frac{u}{\pi\Delta}\right)} = \frac{\mu_B^2}{2\pi\Delta}\left\{1+\frac{u}{\pi\Delta}+\left(\frac{u}{\pi\Delta}\right)^2+\left(\frac{u}{\pi\Delta}\right)^3+\ldots\right\} \qquad (3.33)$$

It is evident that the LSF theory overestimates the amplitudes of the third and fourth order terms by a factor of about 5 and 6. It is interesting to note that the obtained static susceptibility is in fairly good agreement with the exponential form $\chi \sim \frac{1}{\pi\Delta} exp\left\{\frac{u}{\pi\Delta}\right\}$ x surprisingly derived by Iche (1973) in his first parquet approximation. The reason of this surprisingly good agreement should be the subject of futher investitagions.

The comparison of the results given by equations (3.31 - 3.33) confirms our previous conclusions that the enhancement factor appearing in the expression (3.25) of the effective Coulomb interaction is not relevant

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xFootnote.
This expression reminds of the form of inverse Kondo temperature derived in the opposite limit, $\frac{u}{\pi\Delta} \gg 1$ by using the Schrieffer-Wollf transformation, (see section 4.8) but Iche's expression is inversely proportional to Δ instead of the conduction electron band width. The similar analytical form supports the idea which will be discussed in the following section that the physical quantities should be expressed by formulae analytical in the coupling u .

in the behaviour of measurable quantities and that the concept of localized spin fluctuation is not well established.

3.4 Correlation effects in the magnetic limit

The starting point of the previous treatment was to consider first the s-d mixing and then to apply perturbation theory for the intraatomic Coulomb repulsion U assuming that $U \ll \Delta$. This approach is not approriate if the impurity has a well established magnetic moment. In the case of magnetic impurity first the Coulomb term U should be considered in order to produce the splitting of the impurity levels and afterwards the effect of the mixing term can be treated as perturbation. This schema works if $\frac{U}{\pi\Delta} \gg 1$ thus the overlap of the split impurity level is very small. This problem has been worked out in great detail and the results obtained are related to those provided by the s-d model, therefore, here we refer to the next chapter dealing with this problem. The connection between the results of this perturbation procedure and of the s-d model is established by the Schrieffer-Wolff transformation (Schrieffer-Wolff 1966, see section 4.8).

The typical feature of these results is the appearance of a logarithmoc term which looks as $\ln \frac{kT}{D\exp\{\pi\varepsilon_d/\Delta\}}$ in the limit $U \to \infty$ where D is the width of the conduction band.

This logarithmic expression characterizes the Kondo effect and will be discussed in the following chapter in detail.

3.5 General results in the Anderson model at zero temperature.

This section is devoted to a series of such arguments and results which seem to be valid generally and some of them are even exact. These results are of great importance in understanding the behaviour of magnetic impurities at zero temperature even if a few of them has drawn relatively moderate attention until now.

(i) analiticity in coupling strength

By changing the coupling constant U a sharp transition occurs in the HF approximation between the non-magnetic and magnetic regims. In Schrieffer and Mattis theory (1965) ~~for the low density case,~~ it is pointed out that the transition from non-magnetic to magnetic state is completely smooth at least in the investigated (low density) case. Later Suhl (1967) and several other authors argued in the following way. If one considers a phase transition in system with dimension lower than three a sharp transition does not occur because of the strong fluctuadions. Studying the dependence on the coupling strength U one may adopt this idea concluding that the change in the behaviour of a single impurity must

be smooth and analytical even in the region where in lower approximations like in HF a sharp transition takes place.

(ii) dominance of the non-spin-flip scattering channel in the vicinity of Fermi level.

As it has been previously discussed in section 3.2 the dynamical part of the impurity problem is localized on the impurity level. Schrieffer and Mattis (1965) have pointed out that this problem is identical with a problem where there is an interacting electron gas with Lorentzian density of states given by equation (3.3) and Coulomb interaction between electrons with opposite spins, but momentum conservation is not required.

This can be checked by looking the rules of diagram technique. Not much later, Langreth (1966) exploited this idea in many respects pointing out that the most useful consequence of this equivalence is the fact that in the vicinity of the Fermi level a many body system behaves like a free electron gas. This reflects ~~the fact~~ that any kind of decay of a single excitation into a state containing several e.g. n excitations tends to zero like E^{n-1} as the energy E approaches the Fermi level, because the phase space

is strongly reduced as the number of excitations increases in the final state.

In order to put this conclusion in a mathematical form we should consider the one-electron Green's function which has the general expression

$$G_{d,\sigma}(\omega) = \frac{1}{\omega - \varepsilon_d - \Sigma_d(\omega) + i\Delta} \quad , \quad (3.34)$$

where the effect of the "many body correlations" due to the Coulomb interaction is represented by the self-energy $\Sigma_d(\omega)$.

Neglecting Σ_d this formula reduces to equation (3.3). According to the general theorem discussed above $Im\,\Sigma_d(\omega)$ representing the decay processes vaniches at the Fermi level i.e.

$$Im\,\Sigma_d(\omega=0) = 0 \quad (3.35)$$

which can be proved in arbitrary order of the perturbation theory (Luttinger 1960).

(iii) The scattering amplitude at the Fermi level can be expressed in terms of phase shifts at $T = 0$.

The results derived in (ii) and given by equations (3.34) and (3.35) can be inserted into the expression (3.5) of the scattering amplitude and then one obtains

$$t_{kk',\sigma}(\omega=0+i\delta) = V_{kd}\,\frac{1}{\omega-\varepsilon_d-\mathrm{Re}\,\Sigma_{d,\sigma}(\omega)+i\Delta}\,V_{dk'} = \frac{1}{\pi\rho_0}\,\frac{\Delta}{\omega-(\varepsilon_d+\mathrm{Re}\,\Sigma_{d,\sigma}(\omega=0))+i\Delta}\,. \tag{3.36}$$

It is easily seen that the conduction electron scattering amplitude can be given in terms of a single phase shift at the Fermi level if one compares our recent result (3.36) with that in HF approximation which was obtained by inserting equation (3.2) into the form of $t_{kk'}$, given by equation (3.5) then the two forms are identical if $E_{d,\sigma}$ is replaced by $\varepsilon_d + \mathrm{Re}\,\Sigma_{d,\sigma}^{(\omega=0)}$. Thus the scattering amplitude can be expressed in terms of a single phase shift like in HF approximation (see equation 3.17), thus

$$\delta_\sigma(\omega=0) = \mathrm{ctg}^{-1}\left(\frac{\varepsilon_d+\mathrm{Re}\,\Sigma_{d,\sigma}^{(\omega=0)}}{\Delta}\right). \tag{3.37}$$

This means that the elastic non-spin-flip scattering channel being the only one which is open at the Fermi level at $T=0$ the scattering can be characterized by a phase shift.

(iv) Friedel sume rule at $T=0$.

After deriving the results listed in (ii) and (iii) Langreth (1966) has given a general rigorous derivation of the Friedel sume rule. The general form of the sume rule assuming that the scattering can be described

in terms of phase shifts express the total number N of extra electrons associated with the impurity in terms of phase shifts as

$$N = \frac{1}{\pi} \sum_{lm\sigma} \delta_{lm\sigma} (\omega = 0) \qquad (3.38)$$

where $\delta_{lm\sigma}$ is the phase shift in the angular momentum channel l with azimutal quantum number m and spin σ In a different way Anderson and McMillan (1967) have found another exact derivation for the sum rule, furthermore, Langer and Ambegaokar (1961) have concluded that the electron-electron interaction in the conduction band can not affect the sum rule.

In the following we will assume that only the channel with l=2 contributes to the sum rule and the other phase shifts can be neglected.

(v) at $T=0$ the phase shifts are independent of m and σ in the dominant scattering channel $l=2$.

Supposing that no external field is applied and making use of (i) saying that the Coulomb interaction can be continuously switched on, one can conclude that the ground state must be rotational invariant /singlet/ because for $U=0$ the non-magnetic state is rotational invariant. In the case of a singlet state the phase

shifts in each angular momentum channel are equal thus they depend only on ℓ , but are independent of m and σ . Mattis (1967) and Schrieffer and Mattis (1965) have made several attempt to prove that the ground state is indeed singlet i.e. rotational invariant and they could to make it at least very plausible. Furthermore, Anderson (1967/a) argued that a ground state for the impurity must be build up from a linear combination of different states in order to assure the rotational invariance. Finally, the experimental facts to be discussed later show that the magnetic moment associated with the impurity disappears at zero temperature, thus the ground state is indeed singlet.

(vi) If the sbattering channel with l=2 dominates then

$$\delta_{\ell=2} = \frac{\pi N}{10} \quad \text{at} \quad T = 0 .$$

Assuming that at zero temperature the impurity charge is screened completely and in the case of impurities of d -type only the channel with l=2 contributes essentially to the Friedel sum rule given by equation (3.38), one obtains for the phase shifts

$$\delta_\ell = \begin{cases} \frac{\pi N}{10} & \ell = 2 \\ 0 & \ell \neq 2 \end{cases} \qquad (3.39)$$

and than can be referred to as a consequence of "charge neutrality".

The "charge neutrality" implies a series of predictions on those measurable quantities which at $T = 0$ can be expressed by the value of scattering amplitude taken at the Fermi level.

By inserting the phase shift given by equation (3.39) into the formulae (3.16) and (3.8) of the scattering amplitude one obtains that

$$t_{kk}(\omega = 0 + i\delta) = t_{\ell=2}(\omega = 0 + i\delta) = \frac{5}{\pi\rho_0}\left\{e^{i\frac{\pi N}{10}} \sin\frac{\pi N}{10}\right\} \quad (3.40)$$

According to equation (3.22) the zero temperature resistivity can be obtained as a function of N as

$$R(T = 0) \sim \frac{5}{\pi\rho_0} \sin^2\left(\frac{\pi N}{10}\right) \quad . \quad (3.41)$$

Deviation from this formula can be expected if the contributions of the other scattering channels are not negligable. This result does not depend on whether the system behaves magnetic or non-magnetic in HF approximation as it has been pointed out by Grüner and Zawadowski (1972). For non-magnetic impurities in HF sense this formula has been accepted for a long time, (see e.g. Schieffer 1967), however, for magnetic impuries there is some confusion in the

literature. Namely, Schrieffer (1967) has studied the magnetic case with a crystalline splitting of the d-levels larger than their width Δ , and then he has drawn the conclusion that the phase shifts can be different for different orbitals in the same angular momentum channel in contrary to (v). The width of the d-level, however, is so large, that the crystalline splitting can be neglected, therefore Schrieffer's argument is not adequate to 3d-impuries, but it can be applied to 4f-impurities.

3.6 Hartre-Fock picture versus singlet groundstate at $T=0$.

In this chapter we have argued along two different lines using HF approximation and the assumption of a singlet ground state. The results of the two approaches are essentially different in the magnetic limit.

At high temperatures the many-body correlation effects are not strong enough to result in an essential modification of the HF results. In the HF theory if the total density of states for the localied electrons is split exhibiting two fairly well separated peaks then the conduction electron scattering is described with two different phase shifts δ_σ and $\delta_{-\sigma}$.

Thus, in the absence of external magnetic field the magnetic moment of the impurity orbital can be directed parallel or antiparallel to the spin of the incoming electron and the two different phase shifts correspond to these possibilities.Therefore in the conduction electron scattering there is not an uniquely defined phase shift but rather there is a choice between δ_σ and $\delta_{-\sigma}$ with the same probability. On the contrary, however, at zero temperature there is a well defined single phase shift $\delta = \frac{\pi N}{10}$ which is formed as a consequence of many body correlation effects, thus $\delta = \frac{1}{2}(\delta_\sigma + \delta_{-\sigma})$.

Turning to the shape of the total density of states it is represented in figure 6. in a schematic way. The Fermi levels are given for Cr, Mn and Fe impurities respectively, for all cases it can be found between the two peaks. Furthermore using the result of the charge neutrality limit by making use of equations (3.40), (3,6)and finally (3.1) one obtains for the density of states at the Fermi level

$$\rho_d(0) = \frac{1}{\pi\Delta} \sin^2\left(\frac{\pi N}{10}\right) \qquad (3.42)$$

$\rho_d(0)$ is plotted in figure 6 as small circles for different impurities with $N = 4$,5and 6 for Cr,

Mn and Fe. These are far from the density of states predicted on the basis of HF theory, and the question to be answered is how the total density of states obtained from the HF approximation should be modified at low temperature to reach the predicted "charge neutrality" values at E_F for $T = 0$.

In principle there are two possibilities to resolve this problem (see Grüner and Zawadowski 1972).

(i) At low temperatures the density of states changes in that way that at $T=0$ the total density of states is going to exhibit a single maximum corresponding to the non-magnetic HF solution shown in figure 7/a. This would mean a large reordering if the density of states on energy scale of U and Δ i.e. on scale of the order of 1 eV, which is associated with 10^4 ^oK and, therefore no drastic effect can be expected in the temperature range available in experiments.

(ii) At low temperatures an additional peak appears due to correlation effect superimposed on the HF density of states. The width of this resonance is relatively narrow on HF scale and is formed at the Fermi level as it is shown in figure 7/b. The maximum of this narrow peak is determined by the "charge

neutrality" condition. Reminding the relation between density of states and scattering amplitude given by equation (3.6) one can speak about a narrow resonance formed at the Fermi level. As it will be discussed later this narrow resonance is very likely connected to the Kondo effect which is discussed in chapter 4 and in that case the resonance is referred to as Abrikosov-Suhl resonance.

4. KONDO EFFECT AND s-d MODEL

The most striking discovery in the subject has been made by Kondo in 1964, who realized by calculating the conduction electron scattering amplitude of a conduction electron scattered by an impurity spin in the s-d model, that the result diverges at the Fermi level as $ln \frac{\omega}{D}$ in third order of the perturbation theory, where ω is the energy of the conduction electron and D is the width of the conduction band. According to this calculation the impurity resistivity due to a magnetic impurity must increase by lowering the temperature as it has been observed for many years (see e.g. van den Berg G.J. 1964) .This result has suggested that some kind of resonance is formed at the Fermi level which cannot be described by applying simple perturbational method at zero temperature.

The formation of this resonance might resolve the question raised at the end of the previous chapter about the behaviour of the density of states for magnetic impurities at $T = 0$

4.1 s-d model

This simple model, usually, referred to as s-d exchange model is based on the supposition that if a magnetic moment is formed at the impurity than the moment can be described as a quantummechanical spin with quantized total angular momentum $\sqrt{S(S+1)}$, where $S = 1/2, 1, 3/2, \ldots$. In the present case this spin is embedded into a simple metal and an effective exchangeinteraction couples the conduction electron and impurity spins. Similar models have previously been applied to different problems. The basic idea of the model goes back to Zener (1951) who assumed that in ferromagnets the s-electrons form the conduction band and the d-levels are localized at the atomic sites; the s- and d-electrons are interacting by exchange interaction. A similar model has been proposed by Fröhlich and Nabarro (1940) for the exchange interaction between nuclear moments and the conduction electron spins in a metal. Later on Ruderman and Kittel (1954) has applied this model to describe the interaction of two nuclear spins through the conduction band. Similar calculations have also been performed

by Kasuya (1956) and Yosida (1957) in the s-d model.

The derivation of the model was given by Kasuya (1956)

The s-d Hamiltonian can be written as

$$H = H_0 + H_1 \qquad (4.1)$$

where

$$H_0 = \sum_{k,\alpha} \varepsilon_k a^{+}_{k\alpha} a_{k\alpha} \qquad \alpha = \pm 1/2 \qquad (4.2)$$

and

$$H_1 = -\sum_{k,k',\alpha,\alpha'} \frac{\mathcal{J}_{kk'}}{N} \vec{S}\left(a^{+}_{k'\alpha'} \vec{\sigma}_{\alpha'\alpha} a_{k\alpha}\right) \qquad (4.3)$$

ε_k is the energy of the conduction electron with momentum k and spin α. The electrons are described in terms of creation and annihilation operators $a^{+}_{k\alpha}$ and $a_{k\alpha}$. The second term H_1 contains the effective exchange integral $\mathcal{J}_{kk'}/N$, $\vec{S}$ is the impurity spin operator and $\vec{\sigma}$ is the Pauli operator for conduction electron spins. The notation $\mathcal{J}_{kk'}/N$ was introduced by Kasuya (1956) who considered the exchange integral between a Wannier function of the conduction band and the localized d--orbital. N is the number of elementary cells in unit volume and it enters in the calculation as normalization factor at the Bloch wave function expressed by Wannier fundtions. Although the atomic integrals result in a

positive coupling, $\mathcal{J}$ may be negative due to some effective interaction to be discussed in section 4.8 (Schrieffer-Wolff transformation).

The spin product in the Hamiltonian H_1 can be written in a more detailed form as

$$H_1 = -\frac{\mathcal{J}}{N}\sum_{k,k'}\left\{ S^z\left(a^+_{k'\uparrow}a_{k\uparrow} - a_{k'\downarrow}a_{k\downarrow}\right) + \right.$$
$$\left. + S^+ a^+_{k'\downarrow}a_{k\uparrow} + S^- a_{k'\uparrow}{}^+ a_{k\downarrow}\right\} \qquad (4.4)$$

where the first term is the diagonal part of the interaction and the second and third terms correspond to spin flip scattering. The operators S^+ and S^- raise and lower respectively the z-component of the impurity spin.

Generally the exchange integral $\mathcal{J}_{kk'}$ depends on the momenta k and k' and on the angle between them. The usual assumption is that $\mathcal{J}_{kk'}$ does not depend essentially on k and k' and can be taken as constant. This restriction is not serious, because, if $\mathcal{J}_{kk'}$ acts only in some part of the conduction band than ~~one should restrict the consideration only to that part of the conduction band. More generally,~~ the momentum dependence can be formally eliminated by modifying the density of states of the conduction band: i.e. taking a nonvanishing of states only in that range where the interaction is effective. The angular dependence is usually disregarded as well, because it does not effect the final results

in most of the cases..

Supposing that the d-level has the symmetry $\ell=2$ one can find the following angular dependence

$$\mathcal{J}_{kk'} = \mathcal{J}_{\ell=2} \; P_{\ell=2}(\cos\gamma_{kk'}) \qquad (4.5)$$

where P_ℓ is the Legendre polynomial and $\gamma_{kk'}$ is the angle between k and k'.

One can assume, that in addition to the s-d term the impurity represents also a static potential and this interaction is then given by the Hamiltonian

$$H_V = \sum_{k,k',\alpha} \frac{V_{kk'}}{N} a^+_{k'\alpha} a_{k\alpha} \qquad (4.6)$$

where $V_{kk'}$ is the matrix element of the potential.

4.2 Kondo effect in third order of perturbation theory

The first physical quantity calculated beyond the first Born approximation by using the s-d model was the electrical resistivity. In this section we briefly represent the calculation of the electrical resistivity in the first and second Born approximation. It is assumed that the contribution of the impurities to the electrical resistivity is additive, i.e. impurity-impurity

interaction is negligible. In this case the inverse lifetime of the conduction electrons is proportinal to the concentration of the impurities.

The calculation in first Born approximation was carried out by Kasuya (1956) and Yosida (1957)

The probability of spin conserving scattering can be obtained by using the "golden rule" and the first part of the Hamiltonian given by equation (4.4) yields

$$W(\uparrow M_z \rightarrow \uparrow M_z) = 2\pi \left(\frac{J}{N}\right)^2 M_z^2 \rho_0 \qquad (4.7)$$

where ρ_0 is the density of states in the conduction band near the Fermi level and M_z is the z component of the impurity spin. By averaging over the spin direction a factor $S(S+1)/3$ is obtained instead of M_z^2 .

Contribution from the spin-flip terms can be obtained in a similar way

$$W(\uparrow M_z \rightarrow \downarrow M_z+1) = 2\pi \left(\frac{J}{N}\right)^2 [S(S+1) - M_z(M_z+1)]\rho_0 \qquad (4.8)$$

and

$$W(\downarrow M_z \rightarrow \uparrow M_z-1) = 2\pi \left(\frac{J}{N}\right)^2 [S(S+1) - M_z(M_z-1)]\rho_0 \qquad (4.9)$$

The lifetime of a spin up electron (for example) is obtained by adding equation (4.8) and (4.9) together and by averaging over the z-component of the impurity spin M_z . Thus the transition probability

$$W = 2\pi c \left(\frac{J}{N}\right)^2 S(S+1)\rho_0 \qquad (4.10)$$

where c is the concentration of the impurities.

Kondo (1964) performed this calculation in the next order of perturbation theory. The conduction electron scattering amplitude can be calculated in the second order by writing the formula

$$H_1 \frac{1}{\varepsilon_k - H_0} H_1 \qquad (4.11)$$

where ε_k is the energy of the electron in the initial state. The scattering amlitude obtained in this way describes two successiv scattering processes. As far as the intermediate state is concerned there are two possibilities:

(i) first the electron with momentum k is scattered from the initial state into the intermediate state with momentum k' and then this electron with k'' is scattered into the final state with k'.

(ii) in the first scattering process an electron hole pair is created by the spin of the impurity and in the second process the created hole annihilates the electron with momentum k leaving the created electron in the final state.

These processes are represented by diagrams in figures 8/a and 8/b, respectively.

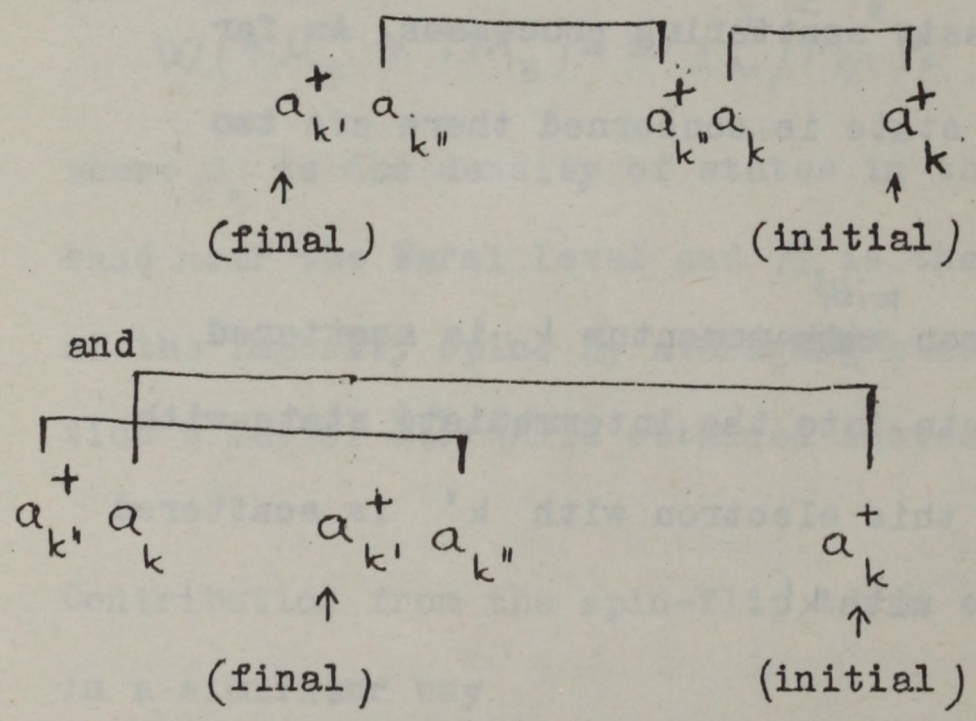
The scattering amplitude for an electron with momentum k'' and spin up is expressed by the following two formulae corresponding to the two diagrams in figure 8.

$$\left(-\frac{J}{N}\right)^2\left\{(S^z)^2+S^-S^+\right\}\sum_{k''}\frac{1-n_{k''}}{\varepsilon_k-\varepsilon_{k''}} \qquad (4.12)$$

and

$$-\left(-\frac{J}{N}\right)^2\left\{(S^z)^2+S^+S^-\right\}\sum_{k'}\frac{n_{k''}}{\varepsilon_k-(\varepsilon_k-\varepsilon_{k''}+\varepsilon_{k'})} \qquad (4.13)$$

where the following pairing of the electron operators are considered



The second expression has a minus sign due to the fermion character of the operators. The occupation number $n_{k''}$ takes care of the Pauli exclusion in the intermediate state.

By adding these two expression two different integrals are obtained

$$\sum_{k''} \frac{1}{\varepsilon - \varepsilon_{k''}} \approx \int d\varepsilon_{k''} \frac{1}{\varepsilon - \varepsilon_{k''}} \rho_0(\varepsilon_{k''}) \qquad (4.14)$$

and

$$g(\varepsilon) = \sum_{k''} \frac{n_{k''}}{\varepsilon - \varepsilon_{k''}} \approx \int d\varepsilon_{k''} \frac{n_{k''}}{\varepsilon - \varepsilon_{k''}} \rho_0(\varepsilon_{k''}) \qquad (4.15)$$

where $\rho_0(\varepsilon_{k''})$ is the density of conduction electrons, and $\varepsilon = \varepsilon_k = \varepsilon_{k'}$ due to energy conservation.

The first integral is small and in the case of symmetric half filled condition band it goes to zero as $\varepsilon \to 0$. The second integral diverges, however, at $T = 0$ as $\varepsilon \to 0$. In order to perform this integral we take a simple form of $\rho_0(\varepsilon)$

$$\rho_0(\varepsilon) = \begin{cases} \rho_0 & \text{if } -D < \varepsilon < D \\ 0 & \text{otherwise} \end{cases} \qquad (4.16)$$

The integral (4.16) can then be calculated for $\varepsilon = 0$ and

$$g(\varepsilon) = -\rho_0 \ln \frac{|\varepsilon|}{(D^2 - \varepsilon^2)^{1/2}} \cong -\rho_0 \ln \frac{|\varepsilon|}{D} \qquad (4.17)$$

for $|\varepsilon| \ll D$. Its temperature dependence can be approximated in a similar way for $\varepsilon = 0$ and one obtains

$$-\rho_0 \ln \frac{kT}{D} + \text{const.} \qquad (4.18)$$

In this way, the inverse relaxation time τ^{-1} can be calculated using equations (4.12), (4.13) and (4.18) and

$$\frac{1}{\tau} \approx 2\pi \rho_0 c \left(\frac{J}{N}\right)^2 S(S+1)\left(1 + \frac{4J}{N} \rho_0 \ln \frac{kT}{D}\right) \qquad (4.19)$$

This formula shows remarkable features: (i) for an antiferromagnetic coupling the inverse relaxation time and therefore the resistivity decreases with increasing temperature (ii) at low temperatures the logarithmic expression dominates and it diverges at $T=0$. The occurrence of this divergency indicates that at low temperatures one should calculate further terms of the perturbation series because the first correction is not small.

It is important to compare this calculation of Kondo with a similar claculation for simple potential scattering. In the latter case spin factors do not occur and in the sum of expressions corresponding to (4.12) and (4.13) the occupation number disappears thus the logarithmic anomaly is specific to magnetic impurities. This is because the potential scattering is a typical one-body problem in contrast to the scattering on a magnetic-impurity, which shows many-body character.

4.3 Kondo effect in leading logarithmic orders

As we have seen in the previous section the first correction to the scattering amplitude is of the order of $(\mathcal{J}/N)\rho_0 \ln(|\varepsilon|/D)$ or $(\mathcal{J}/N)\rho_0 \ln(kT/D)$ $D \gg |\varepsilon| \gg kT$ [illegible] (and $D \gg kT \gg |\varepsilon|$) respectively. These logarithmic term can be so large that $(\mathcal{J}/N)\rho_0 \ln(|\varepsilon|/D)$ is not a small correction even for $\left|\frac{\mathcal{J}}{N}\rho_0\right| \ll 1$.

The terms in the perturbation expansion can be classified according to the following schema

$$\left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho} \ln^{0}(\ )$$
$$\left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho+1} \ln(\ ),\ \left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho+1} \ln^{0}(\ )$$
$$\left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho+2} \ln^{2}(\ ),\ \left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho+2} \ln(\ ),\ \left(\frac{\mathcal{I}}{N}\rho_0\right)^{\rho+2} \ln^{0}(\ ) \qquad (4.20)$$
$$\vdots$$
$$\left(\frac{\mathcal{I}}{N}\rho_0\right)^{n} \ln^{n-\rho}(\ ),\ \left(\frac{\mathcal{I}}{N}\rho_0\right)^{n} \ln^{n-\rho-1}(\ ) \ldots\ldots\ldots \left(\frac{\mathcal{I}}{N}\rho_0\right)^{n} \ln^{0}(\ ).$$

Let us consider some quantity in perturbation theory, and denote the lowest non-vanishing order by ρ e.g. $\rho=1$ for the scattering amplitude and $\rho=2$ for the resistivity. Thus in n^{th} order the highest power of logarithm is $n-\rho$. According to Landau's school the approximation in which we keep only those terms which are in the first column is called logarithmic approximation. The terms in the second column will be referred to as "next to leading logarithmic terms".

We notice by looking at the integral $g(\varepsilon)$ given by equation (4.17) that (i) the shape of the density of states $\rho(\varepsilon)$ does not effect the "leading logarithmic terms", only the next to leading logarithmic terms. (ii) by adding a small imaginary part in the denominator of equations (4.14) and (4.15) results in imaginary terms belonging to the "next to leading logarithmic order".

In this section we briefly review the results obtained in logarithmic approximation. One can derive these results in a straighforward perturbation expansion up to a given order and many of these results can be found in Kondo's review article (Kondo 1969).

In order to carry out these approximations in a more systematic way one should apply diagramatic representation. Whithout any further manipulation, however, the interaction of conduction electron with an impurity spin cannot be represented by diagrams as it can be done for potential scattering. This is due to the fact that the spin is a dynamical variable rather than a static potential. The different states of the spin, however, can be represented by some fictitious particles e.g. fermions, and so one arrives at the different drawn fermion techniques. The most widely applied method is the so called Abrikosov's preudofermion representation Abrikosov (1965) this method has an equivalent form where the spin is represented by a particle with heavy mass /Brenig, Götze, 1968 /. There is a large number of other representations (e.g. Spencer and Doniach 1968) which will not be discussed here.

Let us recall the idea of the Abrikosov's representation. $(2S+1)$ pseudofermions are introduced

~~to represent~~ corresponding to the $2S+1$ states of the impurity spin with z -component $M_z = S, S-1, \ldots -S$. The preudofermions are considered as quantum particles described by creation and annihilation operators, $a^{+}_{M_z}$ and a_{M_z}. An arbitrary spin operator is maped to the preudofermion space according to the relations

$$S \rightarrow \sum_{M_z, M_z'} a^{+}_{M_z'} \langle M_z' | S | M_z \rangle a_{M_z} \qquad (4.21)$$

where the bracket represents the spin matrix elements. The only difficulty remained is that the real spin states are presented by preudofermion states with single occupation, thus ~~the~~ those elements of Hilbert space where more than one pseudofermion states are occupied have no meaning. These states can be eliminated by assuming that the pseudofermions have a large energy $\lambda \gg kT$, furthermore, one can notice that the vacuum state with zero occupation gives no contribution in an actual calculation. In that way all of the results must be normalized to the probability of single occupation $(2S+1)\exp\{-\lambda/kT\}$ with $\lambda \rightarrow \infty$. [x] Usually, in diagrams the solid lines represent electrons and the dotted lines preudofermions.

---

[x] This normalization has recently been proved to be generally correct (Sólyom, Tüttő and Zawadowski 1974) thus the correction term in the previous work by Zawadowski and Fazekas (1969) is incorrect.

It is interesting to note that due to single occupation the interaction vertices are time ordered along the preudofermion line. Therefore, this representation can be simply formulated using time ordered diagrams as well (Brenig, Götze 1968) .

Abrikosov (1965) has pointed out that only those diagrams contribute to the leading logarithmic approximation which by cutting simoultaneously one electron and one preudofermion line fall into two distinct parts and after such successive cuts the elementary vertices are recovered. Therefore in logarithmic approximation the electron-preudofermion scattering amplitude must have the structure as shown in figure 9 , where the diagrams fall into two pieces by cutting one electron and one preudofermion line. This means that only those processes are considered where there is only one excited particle electron or hole in the intermediate state. The diagrams of this type are shown in the two lowest order in figure lo. As it can be shown all the other diagrams contribute to lower powers of the logarithmic term. This class of diagrams is called "parquet" diagrams according to the Russian school and they are calculated with logarithmic accuracy. This method has been worked out by Landau's school in great

detail and the best description of the method is given by Nozieres and his coworkers (Roulet, Gavoret, Nozières 1969 and Nozières, Gavoret, Roulet 1969) .

The general form of the conduction electron scattering amplitude with one electron or hole in the initial and final states can be written as

$$T_{M_z'\alpha',\, M_z\alpha}(\varepsilon) = t(\varepsilon)\delta_{M_z M_z'}\delta_{\alpha\alpha'} + \tau(\varepsilon)\langle M_z'|\vec{S}|M_z\rangle\vec{\sigma}_{\alpha'\alpha} \qquad (4.22)$$

where the energies of the particles in the initial and final states are on the energy shell and the spin variables are α, M_z in the initial and α', M_z' in the final state.

The real part of the scattering amplitude for $\varepsilon = 0$ was obtained by Abrikosov (1965)

$$\tau(\varepsilon=0) = \frac{\frac{J}{N}}{1 - 2\frac{J}{N}\rho_0 \ln\frac{kT}{D}} \qquad (4.23)$$

this term contributes to the leading logarithmic approximations, thus to $\rho = 1$ .The imaginary part of the spin-conserving part of the scattering amplitude

$$\mathrm{Im}\, t\,(\varepsilon=0) = \frac{S(S+1)\left(\frac{J}{N}\right)^2\rho_0}{\left(1 - 2\frac{J}{N}\rho_0 \ln\frac{kT}{D}\right)^2} \qquad (4.24)$$

The resistivity $R(T)$ is proportional to $\mathrm{Im}\, t(\varepsilon=0)$

see optical theorem given by equation (3.22), thus its temperature dependence is

$$R(T) \sim \frac{S(S+1)\left(\frac{J}{N}\right)^2}{\left(1 - 2\frac{J}{N}\rho_0 \ln\frac{kT}{D}\right)^2} \quad . \quad (4.25)$$

In a similar way, the susceptibility was calculated by several authors (see references in Kondo' review 1969) up to a given order. The susceptibility localized on the impurity site is given in this approximation as

$$\lim_{H\to 0} \mu \frac{\langle S^z \rangle}{H} = \mu^2 \frac{S(S+1)}{3kT}\left[1 + \frac{\left(2\frac{J}{N}\rho_0\right)^2 \ln\frac{kT}{D}}{1 - 2\frac{J}{N}\rho_0 \ln\frac{kT}{D}}\right]$$

where the magnetic field H is in the z-direction, and μ is the magnetic moment of the impurity spin. This formula can be derived by using Abrikosov's method (e.g. Zawadowski, Fazekas 1969 [xx] and Ting 1971). Yosida and Okiji (1965) pointed out that the conduction electrons are polarized as well in addition to the Pauli term, however, this contribution appears only in the next the leading logarithmic approximation. Other quantities

[xx] before the logarithmic term a factor of two was missing in that calculation because of the incorrect normalization mentioned in the previous footnote. A large number of papers contain the same mistake (e.g. Yosida, Okiji 1965).

can be calculated in a similar way (see Kondo 1969).

The calculations in logarithmic approximation exhibit drastically different behaviour for ferromagnetic and antiferromagnetic coupling in a crucial manner. Thus, in the ferromagnetic case, the logarithmic expression (4.23) of the scattering amplitude decreares by lowering the temperature. However, in case of an antiferromagnetic coupling this expression diverges as T reaches the temperature T_K, where

$$T_K = D \exp\left\{ \frac{1}{2 \frac{J}{N} \rho_0} \right\} \quad . \quad (4.26)$$

This characteristic temperature is usually called Kondo temperature and $T_K \ll D$ for weak antiferromagnetic coupling, $-1 \ll \frac{J}{N}\rho_0 < 0$. This divergency shows that for $\tilde{\iota}$ the leading logarithmic approximation breaks down as T approaches T_K. The expression (4.26) derived for the characteristic temperature shows a non-analytical behaviour in the coupling J with a strong resemblance to the superconducting transition temperature in the BCS theory. In the theory of superconductivity the similar divergency indicates a phase transition, in the case of a single impurity, however, no phase transition can occur as it has been discussed in section 3.5. It is interesting to note that in the theory for zero temperature, $T = 0$, similar divergency occurs at energy $\varepsilon = k T_K$. Similar behaviour is shown by the susceptibility χ given by equation (4.25). This re-

sult can be written in the form of a Curie-law by introducing an effective moment for the impurity

$$\chi(T) = C \frac{S(S+1)\mu_{eff}^2(T)}{3kT} + \text{Pauli polarization}$$

$$+ 2\frac{J}{N}\rho_0 C \frac{S(S+1)\mu_{eff}^2(T)}{3kT} \qquad (4.27)$$

where

$$\mu_{eff}(T) = \mu\left[1 + \frac{1}{2}\frac{(2\frac{J}{N}\rho_0)^2 \ln\frac{kT}{D}}{1 - 2\frac{J}{N}\rho_0 \ln\frac{kT}{D}}\right]$$

and C is the concentration of the impurities. The last term in expression (4.27) corresponds to the Zener polarization of the conduction electrons which is induced by the polarization of the impurity spins through the exchange interaction. The physical reality of this term is, however, questionable as it will be discussed in section 4.8. According to the first term the effective magnetic moment decreases by lowering the temperature, due to the screening by the conduction electrons. In other words, at low temperatures a strong correlation between the impurity spin and conduction electrons with opposite spin direction is built up. This spin compensation in the conduction electron gas is usually called "spin"compensation cloud". By noticing that only those electrons are strongly scattered by the impurity whose energy is not much further from the Fermi level than the characteristic Kondo energy kT_K, one can realize that the spatial extension of this compensation cloud may be characterized by the length

$$\xi_K = \frac{v_F}{k T_K} \qquad (4.28)$$

which is the coherence length in the Kondo problem; v_F is the Fermi velocity (note the similarity to the coherence length in superconductivity). This compensation cloud and coherence length will be discussed in sections 4.8 and 4.9 in more detail.

Summarising these results one can say that a spurious divergency occurs in most os the quantities if they are calculated in the leading logarithmic approximation. Abrikosov (1965) and Suhl (1965, 1966) have noticed, that the appearance of the singularity indicates the formationnof a resonance in the conduction-electron-impurity scattering amplitude given by equation (4.23), which is centered at the Fermi level. This resonance is called Abrikosov-Suhl resonance. The "leading logarithmic approximation" breaks down as the temperature approaches to the Kondo temperature, and therefore this method is incapable to describe properly this resonance.

There are two ways to improve upon the "leading logarithmic approximation".

(i) to calculate the same diagrams as before with one electron or hole in the intermediate states but with

better accuracy. This means to include the imaginary part of the scattering amplitude and to keep terms in the real part beyond the leading logarithmic approximation.

(ii) to include a wider class of diagrams.

Way (i) will be the subject of the next section while the problem of including more diagrams is left to the chapter 6 dealing with more recent developments in the theory.

4.4 Different methods in the one-particle intermediate state approximation

Soon after the realization of the formation of a resonance at the Fermi energy three different methods have been developed to go beyond the leading logarithmic approximation but keeping only one electron or one hole in the intermediate state. In this section we briefly review these methods:

(i) equation of motion for Green's functions
(ii) dispersion relations
(iii) summation of diagrams

We will not give many details because these methods have already been reviewed by others (see Kondo 1969 and Fisher 1970). Here we present the starting point of the methods and the results obtained will be discussed

in the next section.

(i) equation of motion for Green' functions

Nagaoka (1965) has tried to attact the problem in terms of double-time thermodynamical Green's functions. Following the general method worked out by Bogoliubov's school he studied the equation of motion for the most simple Green's functions. These equations connect the simple Green's function to more complicated ones and a hierarchy of equations can be derived in this way. The basic idea of the method is to cut this hierarchy after some finite step and to approximate the higher order Green's functions in terms of the lower-order ones. Nagaoka started with the one-particle Green's function

$$G(t-t') = -i\,\Theta(t-t')\langle \{ a_{k'\alpha}(t)\, a^{+}_{k\alpha}(t') \}_{+} \rangle \qquad (4.29)$$

where

$$\Theta(t-t') = \begin{cases} 1 & t > t' \\ 0 & t < t' \end{cases} \qquad (4.30)$$

and $a^{+}_{k\alpha}(t)$ is the electron creation operator in Heisenberg representation, furthermore, $\langle \ldots \rangle$ stands for the statistical averrage.

In the next step he considered the Green's functions of type

$$\Gamma(t-t') = -i\Theta(t-t')\langle\{a_{k'\downarrow}(t)\,S^{-}(t),\, a^{+}_{k\uparrow}(t')\}_{+}\rangle \quad (4.31)$$

The Green's functions appearing in the equations of motion of Γ were factorized in the following manner

$$\langle\{a_{k'\uparrow}(t)\; a^{+}_{\ell\uparrow}(t)\; a_{\ell'\downarrow}(t)\, S^{-}(t),\, a^{+}_{k\uparrow}(t')\}_{+}\rangle =$$

$$= \langle\{a_{\ell'\downarrow}(t)\, S^{-}(t),\, a_{k\uparrow}(t')\}_{+}\rangle \langle a_{k'\uparrow}\, a^{+}_{\ell\uparrow}\rangle$$

$$- \langle\{a_{k'\uparrow}(t),\, a^{+}_{k\uparrow}(t')\}_{+}\rangle \langle a^{+}_{\ell\uparrow}\, a_{\ell'\downarrow}\, S^{-}\rangle .$$

By applying this decoupling scheme Nagaoka derived a closed set of equations. These equations can be solved exactly including the imaginary part of Green's functions. Because these equations are singular, their analytical structure had to be treated with special care. The general method to solve singular integral equation of this type is given in Muskhelishvilis book (1953). Following partly the method outlined in this book, the analytic structure of the solution was studied by Hamann (1967), Falk and Fowler (1967), Fowler (1967), Blommfield and Hamann (1967) and finally Zittartz and Müller-Hartmann (1968) gave a general exact solution.

(ii) dispersion relations

Suhl (1965, 1966) realized that this problem has strong resamblance to mezon-nucleon scattering which has been extensively studied in high energy physics. Suhl applied the method of Chew and Low who have derived a closed

set of equations for the scattering amplitude.

Assuming that one considers only those initial and final states in which there is only one electron or hole, the scattering amplitude can be written in the form of equation (4.22), where $t(z)$ and $\tau(z)$ are the amplitudes in the spin-nonflip and the spin-flip channels. The Chew-Low equation derived by Suhl for the scattering on the impurity spin at finite temperature can be written as

$$t(z) = \frac{V}{N} + \int \frac{|t(x+i\varepsilon)|^2 + S(S+1)|\tau(x+i\varepsilon)|^2}{z-x} \rho(x)\,dx \qquad (4.32)$$

$$\tau(z) = \frac{\mathcal{J}}{N} + \int \frac{\tau(x+i\varepsilon)t(x-i\varepsilon) + \tau(x-i\varepsilon)t(x+i\varepsilon) - |\tau(x+i\varepsilon)|^2(1-2n_F(x))}{z-x} \rho(x)\,dx \qquad (4.33)$$

where $\frac{\mathcal{J}}{N}$ and $\frac{V}{N}$ are the exchange and potential scattering amplitudes of the Hamiltonians given by equations (4.3) and (4.6), x is the energy variable on the real axis, $\rho(x)$ is the density of states for conduction electrons. It is important to note that the Fermi distribution functions occurs in the second equation (4.33) only for the spin flip scattering. If only potential scattering is considered, $\tau \equiv 0$ and $n_F(x)$ does not play any role in agreement with our previous discussion in section 4.2 .

These equations were generally solved by Suhl and Wong (1967) . Similar result were also derived by Maleev (1966, 1967).

The approximation applied in the derivation of these equations is that only the one-particle intermediate states are considered. Namely, the scattering processes into and out of the intermediate states are given by the one particle scattering amplitudes $t(z)$ and $\tau(z)$ and the density of states for the intermediate state is replaced by $\rho(x)$.

(iii) summation of diagrams.

Brenig and Götze (1968) considered the parquet diagrams and derived rigorous equations for the scattering amplitude. They solved these equations similarly as in case of methods discussed in (i) and (ii).

It turns out that the three methods discussed above are exactly equivalent. Actually it has been shown by Duke and Silverstein (1967) that the summation of parquet diagrams is equivalent to Suhl's equations. Schotte (1968) and Zittartz (1968) have shown that Suhl's and Nagaoka's equations are also equivalent. Thus all the three methods correspond to the one particle intermediate state approximation which is obvious for the method described in (ii) and (iii) . Although the solution

of these equations are known, it is not trivial in many cases, how to express the physical quantities by $t(z)$ and $\tau(z)$. The general features of the solution and their consequences will be discussed in the following section.

4.5 Results in the one-particle intermediate state approximation and the unitarity limit.

The method discussed in the previous section were aimed to improve upon the leading logarithmic approximation, especially, to include imaginary parts of different quantities. In order to check the accuracy concerning imaginary parts let us discuss the unitarity condition. According to the "optical theorem" the imaginary part of the forward scattering amplitude is proportional to the total cross section and this relation is equivalent to the requirement that the scattering operator is an unitar operator. In the case of Kondo scattering the optical theorem has the following form

$$\mathrm{Im}\, t(x-i\varepsilon) = \pi\rho_0 \left\{ |t(\omega)|^2 + S(S+1)|\tau(\omega)|^2 \right\}$$
$$+ \left\{ \text{one electron or hole + electron-hole pairs in the final state} \right\} \qquad (4.34)$$

All the possible scattering processes contriubte to the right-hand-side of this equation, the spin-conserving and spin dependent scattering channel with one excitation in the final state, furthermore, the other pro-

cesses in which a number of electron-hole pairs as well are created. It is of importance to note that all these contributions are non-negative.

One can see easily that the maximum value of $\mathrm{Im}\, t(\omega)$ is reached in the case [x] when $\mathrm{Re}\, t(\omega)$ and all of the other contributions are zero. This limit is called unitarity limit, where

$$\mathrm{Im}\ t(\omega - i\varepsilon) = \frac{1}{\pi \rho_0} \qquad (4.35)$$

and

$$\mathrm{Re}\, t(\omega) = \tau(\omega) = (\text{contribution of one electron or hole + electron hole pairs}) = 0 \qquad (4.36)$$

Furthermore, the unitarity condition provides an upper limit also for τ , $\tau \leq \frac{1}{2\pi\rho_0} \frac{1}{\sqrt{S(S+1)}}$. This upper bound is strongly violated in the leading logarithmic approximation where τ diverges (see equation 4.23).

The great advantage of the methods discussed in the previous section is that the solutions provided by them

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[x] Footnote

Equation (4.34) can be written as $|\mathrm{Im}\, t(\omega)| = \pi\rho_0 |\mathrm{Im}\, t(\omega)|^2 +$ (positive terms) and the solution of this equation has an upper bound given by equation (4.35) in which case all of the other non-negative terms are zero.

are in agreement with the unitarity condition. Namely, by taking the imaginary part of Suhl's first equation (4.32) one obtaines equation (4.34) but without the contribution of the electron-hole pair creation processes in agreement with our previous statement that these are not included in Suhl's equations. Actually, the unitarity condition is built into the Chew-Low equations at the very beginning.

Furthermore, as it is easy to show, in this approximation the scattering amplitudes must go to the unitarity limit for energy $\omega = 0$ in the case $T = 0$. Let us suppose that $\tau(0+i\varepsilon) \neq 0$, then $\tau(z=0)$ diverges because of the term proportional to $(1-2n_F(x))$ in the second Suhl's equation (4.33) . That divergent contribution is proportional to

$$\int \frac{|\tau(x+i\varepsilon)|^2}{x} \, sg(x) \, \rho(x) \, dx \qquad (4.37)$$

where $sg(x)/x$ is even function of x , thus $\tau(0+i\varepsilon) = 0$

Furthermore, because of the electron hole symmetry $|t(x+i\varepsilon)|^2 = |t(-x+i\varepsilon)|^2$, $|\tau(x+i\varepsilon)|^2 = |\tau(-x+i\varepsilon)|^2$ and $\rho(x) = \rho(-x)$ therefore the right-hand-side of equation (4.32) is pure imaginary, if $V = 0$. Thus, from equation (4.32) one obtains $\mathrm{Im}\, t(0-i\varepsilon) = \frac{1}{\pi \rho_0}$ which is the unitarity limit given by formula (4.35). The case $V \neq 0$ will be discussed in the following section.

We have seen again that the crucial term of Suhl's equation is that one which is proportional to the factor

$(1 - 2n_F(x))$ occuring in the spin-flip scattering term.

The solution has a simple form for $\omega = 0$ at finite temperature $T = 0$ (Hamann 1967).

$$t(\omega + i\varepsilon) = \frac{1}{2\pi i \rho_0}\left[1 - \frac{\ln \frac{T}{T_K}}{\sqrt{\left(\ln \frac{T}{T_K}\right)^2 + S(S+1)\pi^2}}\right] \quad (4.38)$$

and

$$\tau(\omega) = \frac{1}{2\rho_0} \frac{1}{\sqrt{\left(\ln \frac{T}{T_k}\right)^2 + S(S+1)\pi^2}} \quad (4.39)$$

where in the weak coupling limit

$$kT_K \approx D \exp\left\{2\frac{J}{N}\rho_0\right\} \quad (4.40)$$

The energy dependence at $T = 0$ is very similar to the temperature dependence at $\omega = 0$, t is monotonically decrearing starting from the unitarity value at on the other hand $\tau = 0$ at the Fermi energy and exhibits a peak at energy $|\omega| = kT_K$ and then it decreares whith increaring temperature. Considering $Im\, t(\omega)$ at $T = 0$, a resonance is gradually smeared out with increaring temperature.

The solution shows the following features:

(i) the behaviour of the solution is logarithmic at low and high temperature (see equations 4.37 and 4.38) and at small and high energies, as well.

found at the Fermi level, which is symmetric in energy and has a width of kT_K. This resonance is

(ii) $Im\ t$ tends to the unitarity limit as $\frac{\omega}{T_K}$, $\frac{T}{T_K} \to 0$. In this case the scattering is spin conserving at the Fermi level in agreement with the general statement (ii) in section 3.4.

(iii) in the region $T/T_K \gg 1$ or $|\omega|/T_K \gg 1$ the solution is in agreement with those obtained in the leading logarithmic approximation (see equations 4.24 and 4.23).

The impurity resistivity is determined by the temperature dependence of $|Im\, t(\omega)|_{\omega=0}$ as

$$R(T) = \frac{2\pi c}{\rho_0 e^2 k_F} \left\{ 1 - \frac{\ln \frac{T}{T_K}}{\sqrt{\left(\ln \frac{T}{T_K}\right)^2 + S(S+1)\pi^2}} \right\} \quad (4.41)$$

where c is the concentration of the impurities (number in unit volume), k_F is the Fermi momentum and "e" is the electron charge.

The zero temperature resistivity is determined only by the unitarity limit (the expression in the bracket in equation (4.41) is equal 2), and does not depend on the value of spin S.

Similarly to the impurity resistivity, other physical quantities, like susceptibility, heat capacity and the change of entropy ΔS have been calculated on the basis of this approximation. Zittartz (1968/b) determined the susceptibility assuming that the g-factors for conduction electrons and the impurity spin are equal. The following expression was obtained for $\ln \frac{T_K}{T} \gg 1$

$$\chi(T) = \frac{1}{3kT}(g\mu_B)^2 \left[S(S+1) - \left(S+\tfrac{1}{2}\right) + \right.$$

$$\left. + \frac{S(S+1)}{\ln \frac{T_K}{T}} + \text{Pauli term} + O\left(\ln^{-2}\frac{T_K}{T}\right)\right] \quad (4.42)$$

This expression goes to a Curie low at very low temperature. Thus the effective moment $\mu_{eff}(T)$ determined from the susceptibility using equation (4.27) does not disappear as $T \to 0$. In other words, this result does not agree with the expectation that the ground state is singlet and its magnetic moment is zero (see section 3.4).

The heat capacity was also calculated and it exhibits a peak at $T = \frac{1}{3}T_K$ and the energy change related to the formation of the ground state is of order kT_K (Hamann and Bloomfield 1967). According to this result the heat capacity $c(T) \to 0$ with some power of T as $T \to 0$. The entropy change related to the formation of the ground state was calculated as well by Zittartz and Müller-Hartmann (1968) and it was found that

$$\Delta S = -k_B\left[(2S+2)\ln(2S+2) + 2S\ln 2S - 2(2S+1)\ln(2S+1)\right]. \quad (4.43)$$

This result depends on the value of the spin S, it does not show, however, that the transition would place

between a singlet ground state and a free spin with degree of freedom zero and $2S+1$, respectively.

Summarizing the result obtained in the one particle intermediate state approximation one can conclude that at high temperature it reproduces the perturbational result at least in leading logarithmic approximation. At lower temperature it provides an imaginary part to the scattering amplitude in that way that the unitarity condition is satisfied and at zero temperature the scattering amplitude tends to the unitarity limit. However, the other results for low temperatures are very questionable. The problem is left to make clear how much the low temperature behaviour can be effected by including the contributions of the many particle intermediate states. This question can be answered either by comparing the theoretical expressions with the experimental results or on theoretical grounds by using renormalization and scaling arguments. This will be discussed in section 6.

4.6 Kondo effect including potential scattering

The discussion presented in the previous section about the unitarity limit is based on the assumption that the interaction is pure exchange scattering and $V=0$ in the Hamiltonian 4.6 . Actually, the mean features of the formation of resonance is not influenced by the potential scattering, but our conclusion that $Re\, t(\omega)|_{\omega=0} = 0$ for $T=0$, in not generally valid, see the real part of equation (4.32). The problem with potential scattering has been worked out in the framework of Nagaoka,s equation (Fischer 1967,

Schotte 1968 , Kondo 1968, Nagaoka 1969).

The Kondo acattering is very sensitive to the density of states at the impurity site. The potential V changes this density of states and that results in two different effects.

The result can be expressed in term of the conduction electron phase shift δ_V due to the potential scattering. The potential V reduces the density of conduction electrons at the Fermi level by a factor $\cos^2\delta_V$ thus $\frac{J}{N}\rho_0$ must be replaced $\frac{J}{N}\rho_0\cos^2\delta_V$ which can be done in a formal way by introducing and effective exchange interaction

$$\overline{J} = J\cos^2\delta_V \qquad (4.44)$$

Furthermore, in Nagaoka's scheme the resistivity is essentially changed compared to equation (4.41) and (Nagaoka 1969)

$$R(T) = \frac{2\pi c}{\rho_0 e^2 k_F}\left\{2\sin^2\delta_V + \cos 2\delta_V\left[1 - \frac{\ln\frac{T}{T_K}}{\sqrt{\ln\left(\frac{T}{T_K}\right)^2 + S(S+1)\pi^2}}\right]\right\} \qquad (4.45)$$

which is in agreement with equation (4.41) if $\delta_V = 0$. The value of the resistivity at $T = 0$ is reduced by a factor $\cos^2\delta_V$ with respect to the unitarity limit. This result has been derived in the framework of the one-particle intermediate state approximation. However, we emphasized at the end of the previous section that at low temperature this approximation breaks down, therefore the validity of this expression even for $T = 0$ is not well justified.

As it has been first pointed out by Fischer (1967) the sign of the logarithmic terms in the expression of the resistivity depends on δ_V, thus it may be opposite compared to the original Kondo results (where $\delta_V = 0$) if $\delta_V \geq \frac{\pi}{2}$. Furthermore, the potential scattering may result in important effect for thermopower. Namely, if the electron-hole symmetry holds, the Kondo resonance is symmetric to the Fermi level $t(\omega+i\varepsilon) = t(-\omega+i\varepsilon)$, thus the thermopower is zero because it is proportional to the antisymmetric part of the scattering amplitude. The presence of the potential scattering, however, breaks this symmetry and the thermopower is finite.

4.7 Variational calculations for the ground state

We have already discussed the formation of Abrikosov - Suhl resonance in the electron-impurity scattering at law temperatures. At zero temperature several authors have considered this resonance as a bound state built up from the impurity spin and from the conduction electron polarization. This bound state is formed in such way that the total spin of this state is zero thus the conduction electrons screen the impurity spin. Although several attempts have been made to construct a variational wave functions to describe this bound state, these calculations do not lead to better theoretical treatment than those we have described before. The main drawback of these approaches is, that it is hard, or even impossible to estimate the accuracy achieved. However, these attempts lead to a better

understanding the main difficulties and are therefore very instructive.

The first type of methods are the variational calculations of the Japanese group, which is reviewed by Yosida (1971) in considerable detail. In the first step one constructs a wave function in which a single electron is attached to the impurity spin while the other electrons are unperturbed. This wave function can be written in a simple form (see Yosida 1966 / a-b, Okiji 1966 and Heeger and Jensen 1967)

$$\psi_0 = \sum_{k>k_F} \Gamma_k \left(a_{k\downarrow}^{+} \alpha - a_{k\uparrow}^{+} \beta \right) \psi_V \qquad (4.46)$$

where α and β are the spin states with $\sigma_z = 1$ and $\sigma_z = -1$, ψ_V is the wave function of the free electron gas with Fermi momentum k_F. The binding energy E_B is obtained by variational calculation of the coefficient Γ_k and the binding energy is given by

$$E_B = \begin{cases} D \exp\left\{ -\frac{2}{J\rho_0} \right\} & \text{if } J>0 \\ D \exp\left\{ \frac{2}{3} \frac{1}{J\rho_0} \right\} & \text{if } J<0 \end{cases} \qquad (4.47)$$

This result contradits to the expression of Kondo temperature given by equation (4.40) because it gives bound state for ferromagnetic coupling ($J>0$) as well, furthermore the binding energy is smaller than the Kondo temperature T_k given by equation (4.26) as the factor 1/2 in the exponent of Kondo temperature is replaced by 2/3. This result can also be derived using diagrams, and then this simple wave function with one excited electron corresponds to summation of ladder diagrams where the ladder

is formed by a parallel electron and impurity spin lines (see e.g. the first diagrams in figures 1o/a and 1o/b). In this case, the electron and impurity spin forms a bound state with binding energy given above (see e.g. Sólyom 1966) and the exponents obtained are characteristic to the approximations where only diagrams simpler than the "parquet diagrams" are summed up (see discussion in section 4.3). Yosida (1966/a, 1966/b) recognized this problem and he included an additional electron-hole pair into the wave function, which then has the new form

$$\psi = \psi_0 + \sum_{k_1 k_2 k_3} \Gamma^{(1)}_{k_1 k_2 k_3} \left(a^+_{k_1\downarrow} a^+_{k_2\downarrow} a_{k_3\downarrow} \alpha - a^+_{k_1\uparrow} a^+_{k_2\uparrow} a_{k_3\uparrow} \beta \right) \psi_V$$

$$+ \sum_{k_1 k_2 k_3} \Gamma^{(2)}_{k_1 k_2 k_3} \left(a^+_{k_1\uparrow} a^+_{k_2\downarrow} a_{k_3\uparrow} \alpha - a^+_{k_1\downarrow} a^+_{k_2\uparrow} a_{k_3\downarrow} \beta \right) \psi_V . \qquad (4.47)$$

The presence of the electron-hole pair improved the coefficient in exponent of the binding energy, and 0.62 was obtained instead of 2/3, this correction is in the direction to the value of 1/2. This sort of calculation was extended by Yoshimori (1968) who considered an infinite number of electron-hole pairs, and by this way the expected exponent 1/2 was obtained. In this calculation a set of coupled integral equations which was shown by Nakajima (1968) to be equivalent to Abrikosov's vertex-equation with logarithmic occuracy has been solved.[x] Thus the "parquet" or leading logarithmic approximation leads to ground state

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x Note: This type of calculations were extended to the case of external magnetic field as well (see Yosida's review 1971).

where already an infinite number of electron-hole pairs is excited. It was not possible to make further progress along this line without improving the calculation technique in an essentially way. This has been done by Sakurai and Yoshimori (1973) who have built the renormalization group technique into this schema (see Chapter 6).

A different construction of the ground state wave function was given by Kondo (1966) and Appelbaum and Kondo (1968). Without going into a discussion in detail, we only remark, that this attempt was a very good example, how difficult it is to estimate the accuracy of the method (see Hamann and Appelbaum 1969). By now is generally excepted that it is very hard to get reliable information on the properties of the Kondo state by constructing sophisticated ground state wave functions.

Other type of ground state wave functions were suggested starting from the Anderson model and two of them are very instructive. Anderson (1967/a) focused his attention to the construction of a singlet wave function expressed in terms of conduction electron phase shifts which strongly depend on energy. The basic idea has a strong resemblance to the discussion of section 3.6. The starting point is a HF like picture, where the phase shifts $\delta_\uparrow$ and $\delta_\downarrow$ increase

from zero to π in the energy range of the d-level or it remains constant depending whether the d-level with that spin direction is occupied or not. This is in accordance with the Friedel sum-rule in HF approximation (see solid lines in figure 11) . For the ground state, however, the phase shifts provide a correct description of the system at the Fermi level, furthermore, as the ground state is singlet the phase shifts must be the same for the two spin directions (see discussion in section 3.5 and 3.6). Anderson's main idea was to modify the phase shifts occuring in the construction of the ground state wave function in such way that they are altered only in the vicinity of Fermi energy and they are equal at the Fermi energy (see dotted lines in figure 11) . In our general discussion (section 3.6) we argued that the HF picture is essentially correct at large energies or at high temperatures, thus the phase shifts are 0 or π in the energy region between of the d-levels and this is in accordance with the broad structure of the d-level density of states (see figure 6. and 7.). In the discussion of section 3.6 the problem of two phase shifts 0 and π and the uniform phase shift $\frac{\pi}{2}$ at the Fermi energy was resolved by assuming the formation of a resonance at the Fermi level. In order to describe this situation, Anderson modified the phase shifts in the constructed wave function just in the region of the Abrikosov-Suhl resonance.

Finally, a recent work of Okada and Yosida (1973) has to be mentioned, They started from five-fold degenerate impurity levels in the Anderson model and they derived an effective Hamiltonian by applying a transformation of Schrieffer-Wolff type, however, the effective Hamiltonian is more complicated than in the simple s-d model. Further, a ground state wave function was constructed which is a generalization of the procedure reviewed first in this section. The most striking conclusion obtained is that at zero temperature the electrical resistivity is proportional to $\sin^2\left(\frac{N\pi}{10}\right)$ in agreement with the general analysis of the present authors (Grüner and Zawadowski 1972) and with the resistivity formula (3.41), thus this work provides confirmation of the discussion along the section 3.5 and 3.6. This result shows again that studying low temperature properties one should turn to the Anderson model rather than applying the simple s-d model which leads, according to our present knowledge to residual resistivity independent of the spin of the impurity (see equation 4.41).

4.8 Derivation of the s-d model from the Anderson model; Schfrieffer-Wolff transformation.

Along the present chapter the existence of magnetic moment at the impurity site has been taken for granted as the moment is built into the s-d Hamiltonian (4.2).

Previously, on the basis of the Anderson model, however, the necessary condition for formation of the magnetic moment has been discussed in the H.F. approximation where in order to have a moment the intraatomic Coulomb interaction must be large enough, i.e. $U \gg \pi\Delta$. The goal of this section is to find a more rigorous relationship between these two models.

Let us treat the most simple case, where the atomic orbital is nondegenerate. If in the Anderson Hamiltonian given by equation (2.3) $\varepsilon_d < 0, 2\varepsilon_d + U > 0$ then the impurity level is single occupied in the limit $V_{kd} \to 0$. The effect of the s-d mixing V_{kd} which result in the conduction electron scattering on the impurity can be considered as perturbation. This scattering can be treated in the second order of perturbation theory as

$$H_V \frac{1}{E_i - E_m} H_V \qquad (4.48)$$

where H_V is the mixing term of the Hamiltonian (2.3), transition rate is given by V_{kd}, E_i and E_m are the energies of the initial and intermediate states, respectivelly. Let us assume, that there is one exited conduction electron with energy ε_k in the initial state and the impurity level is single occupied and so $E_i = \varepsilon_k + \varepsilon_d$ The scattering can occur through two different intermediate states

(i) first the conduction electron jumps on the d-level to make it double occupied with energy $E_m = 2\varepsilon_d + U$

(ii) the d-level becomes first empty by exciting a con'uction electron with momentum k' and in the second step the exited conduction electron occupies it, thus $E_m = \varepsilon_k + \varepsilon_{k'}$. These processes are shown in figure 12. In the final state the impurity level is single occupied and one conduction electron is in the excited state with momentum k'. The transition may be spin--flip and spin-conserving scattering, which can be formally described by the [illegible] Hamiltonian given by equations (4.3) and (4.6). The coupling strengths $\mathcal{J}_{kk'}$ and $V_{kk'}$ can be chosen to fit the transition amplitudes obtained in the Anderson model, and then

$$\frac{\mathcal{J}_{kk'}}{N} = V_{kd} V_{dk'} \left\{ \frac{1}{\varepsilon_k - \varepsilon_d - U} + \frac{1}{\varepsilon_d - \varepsilon_{k'}} \right\} \qquad (4.49)$$

and

$$\frac{V_{kk'}}{N} = \frac{1}{2} V_{kd} V_{dk'} \left\{ \frac{1}{\varepsilon_k - \varepsilon_d - U} - \frac{1}{\varepsilon_d - \varepsilon_{k'}} \right\}$$

where the two denominators correspond to the two different intermediate states. As only those matrix elements are of importance in the Kondo effect in which the excited conduction electron energies are near the Fermi level, $\varepsilon_k, \varepsilon_{k'} \approx 0$. In this way the expressions for $\mathcal{J}_{kk'}$ and $V_{kk'}$, are simplified to

$$\frac{\mathcal{J}}{N} = -|V_{kd}|^2 \frac{U}{|\varepsilon_d|(U - |\varepsilon_d|)} < 0 \qquad (4.50)$$

and

$$\frac{V}{N} = \frac{1}{2} |V_{kd}|^2 \frac{U - 2|\varepsilon_d|}{|\varepsilon_d|(U - |\varepsilon_d|)} > 0 \qquad (4.51)$$

Thus the effective exchange interaction due to these processes is always negative. These expressions has been first derived by Clogston and Anderson (1965)

and Kondo (1962). A canonical transformation was applied by Schrieffer and Wolff (1966) in order to arrive at the above result, whose generator S is given by

$$S = \left\{ \sum_{k,\sigma} \frac{V_{kd}}{\varepsilon_k - \varepsilon_d - U} n_{d-\sigma} a^{+}_{k\sigma} a_{d\sigma} + \sum_{k,\sigma} \frac{V_{kd}}{\varepsilon_k - \varepsilon_d} (1 - n_{d-\sigma}) a^{+}_{k\sigma} a_{d\sigma} \right\} - \{ c.c. \} \qquad (4.52)$$

and the new form of the Hamiltonian is $e^{S} H e^{-S}$. These result were generalized by Schrieffer (1967) and Mühlschlegel (1968) for the degenerate Anderson model and for this situation the result given in equation (4.50) was modified by a factor $\frac{1}{2S}$ where S is the spin of the impurity. This general relationship between the s-d and Anderson model is usually quoted as Schrieffer-Wolff transformation in the literature.

Several physical quantities (e.g. resistivity, susceptibility) have been calculated in fromework of the Anderson model by carrying out a perturbation expansion in V_{kd} (e.g. Scalapino 1966, Dworin 1967 and Hamann 1966). In these calculations as it has already been mentioned in section 3.4 it is assumed that $U, |\varepsilon_d| \gg \Delta$ and the logarithmic approximation is applied. The most careful comparison of the results in the Anderson model with those obtained using s-d model was performed by Keiter and Kimball (1971) who found that, in general, the leading logarithmic contributions can be calculated correctly on basis of the s-d model with exchange coupling given by equation (4.50), though the further terms are rather dubious. Furthermore, the assumption $U \gg \Delta$ plays an important role, because it means

that the splitted d-levels are far from the Fermi level and their tails can be neglected in the region. This assumption is certainly fulfilled for Mn impurities in Cu, Ag and Au host and less for Al host where Δ is larger. This is, however, not the case for other impurities Fe and Cr for example because the d-levels are partially occupied and the density is quite large at the Fermi level. In other words, either $|\varepsilon_d| \gg \Delta$ or $|\varepsilon_d + u| \gg \Delta$ does not hold. Furthermore, it is obvious that the Schrieffer-Wolff transformation is valid for rather large u/Δ values, and breaks dow progressively with decreasing u/Δ .

So far the discussion was limited to the comparison of the scattering amplitudes obtained in the two models. Looking at the form of Schrieffer-Wolff transformation (equation 4.52) however, the question how this transformation mixes the s- and d-states can be raized.
In a recent paper Stewart and Grüner (1973) calculated the magnetic moment M of the impurity in the limit $|\varepsilon_d|, |\varepsilon_d + u| \gg \Delta$ by using the H.F. approximation, when the overlap of the d-levels are small. The result is

$$M = \mu_B \left(\langle n_{d\uparrow}\rangle - \langle n_{d\downarrow}\rangle\right) = \mu_B \left\{\left(1 - \frac{1}{\pi}\frac{\Delta}{|\varepsilon_d|}\right) - \left(\frac{1}{\pi}\frac{\Delta}{u+\varepsilon_d}\right)\right\} =$$

$$= \mu_B \left(1 - \frac{|\mathcal{J}|}{N}\rho_0\right) \qquad (4.53)$$

where the first expression comes from the asymptotic expansion of equation (3.11)and the second form is obtained by using the Schrieffer-Wolff transformation (4.48)and

equation (3.1) for Δ . Moreover, in the susceptibility the factor $M^2 \sim (1-|J|N^{-1}\rho_0)^2 \sim (1-2|J|N^{-1}\rho_0)$ occurs. As it was already mentioned the susceptibility is completely localized to the d-level in H.F. approximation (see Anderson's compensation theorem is section 3.2). In contrary to this result in the s-d model the first correction to the susceptibility is the Zener term, which has exactly the same amplitude (see equation 4.27) but it is located at the conduction band. This discrapancy was studied by Grüner and Zawadowski (1974) who found that it is the artifact of Scrieffer-Wolff transformation which - although conserves the total momentum - mixes the d-level and conduction band polarizations. With respect to localization the main features of this transformation can be summarized in the following way. In H.F. approximation the total momentum is localized to the d-level and is less than what would correspond to $S = 1/2$, therefore it can not be described by a spin operator. By means of the Schrieffer-Wolff transformation a new set of d- and conduction-electron states are introduced by the new annihilation operators $\bar{a}_{k\sigma} = e^{S} a_{k\sigma} e^{-S}$ and $\bar{a}_{d\sigma} = e^{S} a_{d\sigma} e^{-S}$ and the new states are not completely localized to the d-level and to the condution band, thus they are slightly mixed into one other. In the new representation the momentum on the d-level is increased by the factor $(1-2|J|N^{-1}\rho_0)^{-1}$ to achieve a localized spin with $S = 1/2$. As the total spin is conserved a spin deficit occours in the conduction band, which is the wellknown Zener term. The conclusion therefore is, that the occurance of the Zener term in dilute alloy

problem is artificial and is entirely due to the assumption that a spin with half-integer value is formed on the impurity site. Although this consideration is limited to H.F. approximation, it implies that the distinction between the spin and conduction band is somewhat artificial in the s-d model.

4.9 Conduction electron density of states and charge oscillation around the impurities.

Friedel (1954) has first pointed out that impurities in metals perturbe the conduction electron states. This perturbation is called the Friedel oscillation, and at large distances r (the charge perturbation $\Delta\rho(r)$) has the asymptotic form

$$\Delta\rho(r) = -\frac{(2\ell+1)\sin\delta_\ell(0)}{4\pi^2 r^3}\cos(2k_F r - \ell\pi + \delta_\ell(0)) \quad (4.54)$$

where r is measured from the impurity site, ℓ is the angular momentum quantum number (in general there is a summation over ℓ). The conduction electron density of states can be calculated from the one particle Green's function G which is expressed by the unperturbed Green's function $G^{(0)}$ and by the spin conserving part of the scattering amplitude t as $G = G^{(0)} + G^{(0)} t G^{(0)}$. We have seen previously that at $T = 0$ and at the Fermi energy this scattering amplitude can be given in terms of phase shifts ($\delta_\ell(0)$) (see section 3.5) and this phase shift enters in the expression (4.54).

Recently a series of calculations have been performed to investigate the preasymptotic behaviour of this perturbation. The most detailed study of the density

of states $\rho(r,\omega)$ at energy ω measured from ε_F is given by Mezei and Zawadowski (1971/a). Three characteristic distances are important for this behaviour: (i) the atomic distance $(\sim k_F^{-1})$ and two coherence lengths (ii) $\xi_\omega = \frac{v_F}{\omega}$ and (iii) $\xi_{\Delta'} = \frac{v_F}{\Delta'}$ where Δ' is a characteristic energy related to the momentum dependence of the scattering amplitude, v_F is the Fermi velocity ($\Delta' \sim v_F \delta k$ where δk is the momentum region in which the scattering amplitude ~~depends on the momentum~~ is large). The energy Δ' must be in the order of the broadened atomic energy levels, thus $\xi_{\Delta'}$ should be of around 5-1o Å. This quantity may be important in the case of tunnel junctions with an impurity layer (Mezei and Zawadowski 1971/b), but not in the present context.

In experiments the charge oscillation, rather than the density of states is important. The two quantities are related by

$$\rho(r) = \int_{-\varepsilon_F}^{0} \rho(r,\omega)\, d\omega \qquad (4.55)$$

In $\rho(r)$ the energy dependence of the spin-conserving scattering amplitude $t(\omega)$ has a crucial role. In order to study this effect, Mezei and Grüner (1972) considered a free electron gas with one impurity which is a simple resonant scatterer, in this case the scattering amplitude has the form

$$t_e(\omega) = \frac{1}{\pi \rho_o} \frac{\Delta}{\omega - \omega_o + i\Delta} \qquad (4.56)$$

in the angular momentum channel $\ell=2$, where Δ is the width, ω_0 the position of the resonance. The charge perturbation is written in the form

$$\Delta\rho(r,\omega) = -\frac{(2\ell+1)}{4\pi^2}\sin\delta_\ell(0)\cdot\frac{a(r)}{r^3}\cos(2k_Fr-\ell\pi+\delta_\ell(0)+2\varphi(k_Fr)- \\ -\eta(r)\} \qquad (4.57)$$

where the derivation from the assymptotic form (4.54) is expressed in terms of $a(r)$ and $2\varphi(k_Fr)-\eta(r)$ [x] which describe the radial dependence of the amplitude and phase respectively. The function $a(r)$ is plotted in figure 14. for different values of ω_0. One can see, that for $r<\xi_\Delta=\frac{v_F}{\Delta}$ there is a strong reduction in the amplitude, and - on the other hand - in the asymptotic region $r\to\infty$ $a(r)\to 1$ and reproduces expression (4.54). In the case of our interest Δ is of the order of $1eV$, therefore $\xi_\Delta\sim 10\,\text{Å}$ and should be measurable by experiment.

In the case of Kondo effect, the narrow resonance appearing in the scattering amplitude should show up in the charge perturbation in an essential way as the width kT_K of this resonance can be small, therefore the corresponding coherence length ξ_{kT_K} rather large. Although the detailed radial depencende depends on the form of the Suhl-Abrikosov resonance, the main effect is the reduction of the ocsillation amplitude at distances $r<\xi_{kT_K}$. Indeed, calculation of $\rho(r)$ on the basis of the s-d model (Bloomfield et al 1970, Klein 1969) shows this reduction near to the impurities. $\rho(r)$ obtained in this way is shown in figure 14.; far from

[+] For the meaning of $\varphi(k_Fr)$ and $a(r)$ see the original publication (Mezei and Grüner 1972).

the impurities $\rho(r)$ goes as r^{-3} , but saturates near to the impurity, this saturation is the consequence of the reduced amplitude. The overall behaviour is the same as that calculated by Mezei and Grüner (1973), if Δ is replaced by kT_K .

These results can be formulated in a more general way. Let us consider some arbitrary scattering amplitude shown in figure 15., which has a structure with a characteristic width $\delta\omega$ in the region near to the Fermi energy. Looking for the effect of this structure in the charge oscillation one can find, that at distances $r \gg \xi_{\delta\omega}$ this structure ~~has no essential on the~~ contributes to the charge oscillation amplitude ~~which~~ as it is determined by $t(o)$ only. At distances $r \ll \xi_{\delta\omega}$ however this structure does not contribute to the charge perturbation. In other words at distances r one observes the effect of a scattering amplitude $\bar{t}(\omega)$ smeared out at an energy scale $\delta\omega$ where $r \sim \xi_{\delta\omega}$. In this way the pre-asymptotic behaviour of the charge perturbation is a powerful tool for studying the shape and width of the resonances.

An other advantage of the charge perturbation is, that the temperature dependence of the oscillation amplitude in the asymptotic region is determined only by the temperature dependence of $t(o)$, in contrast to the transport properties where the energy and temperature dependence is mixed together (Grüner and Hargitai 1971).

4.1o Spin perturbation in the s-d model and the spin compensation cloud.

In section 4.8 the various contriubtions to the magnetic moment were discussed. In the s-d model, the term $-\frac{J}{N}\rho_o$ in equation (4.53) is the consequence of the polarization of the electron gas by the impurity spin. This polarization however is not uniform, but decreases going away from the impurity and has an oscillatory form similarly to the charge perturbation. In the H.F. approximation of the Anderson model this spin perturbation is simply the difference between the charge perturbations for the spin up and spin down conduction electrons. For a well split virtual bound state this perturbation has the form

$$\Delta\sigma(r) = \frac{\alpha'}{r^3}\cos(2k_F r + \varphi') \qquad (4.58)$$

with

$$\alpha'\cos\varphi' = (\sin\delta_\uparrow\cos\delta_\uparrow - \sin\delta_\downarrow\cos\delta_\downarrow)$$
$$\varphi'\sin\varphi' = (\sin^2\delta_\uparrow - \sin^2\delta_\downarrow) \qquad (4.59)$$

From the s-d model one arrives at a similar radial dependence, and then the spin perturbation has the well known Rudermann-Kittel-Kasuya-Yoshida (RKKY) form

$$\Delta\sigma(r) = \frac{J}{N}\rho_o\,\frac{r\cos(2k_F r) - \sin(2k_F r)}{r^4} \qquad (4.6o)$$

which reduces to a $\frac{\cos 2k_F r}{r^3}$ form at large r values. Comparing the amplitudes in equations (4.58) and (4.6o) one immediately arrives at the Schrieffer-Wolff result (given by equation (4.5O)) (Blandin 1967).

It was also shown is section 4.8 that a finite s-band

polarization is probably artificial and the integral over r of equation (4.60) should be zero instead of $\frac{\mp}{N}\rho_0$. Therefore the radial dependence should be slightly modified, this modification shall be the most dominant near to the impurities (see for example Geldart 1972).

Naturally, the Kondo effect should modify the above results, as the singlet state itself is the result of a spin correlation. The static magnetic susceptibility has been discussed in 4.3. The main feature of the results presented there are that at very high temperatures $T \gg T_K$ the spin is practically uncoupled to the conduction electron, but by lowering the temperature, the sceening of the magnetic moment of the impurity by polarization of the conduction band set in at $T > T_K$, below the Kondo temperature on the other hand the screening becomes stronger and at $T=0$ on the basis of general arguments (see section 3.5) a singlet ground state, i.e. a complete screening occurs. In the region $T > T_K$ the perturbation theory with logarithmic accuracy is appropriate, at $T \sim T_K$ however, the approximation with one particle in the intermediate state breaks down and fails to predict a singlet ground state. (see equation 4.42) This singlet ground state can be visualized in such a way that the impurity spin is rigidly coupled to the screening spin polarization cloud and this coupled system is rotating. This polarization cloud is frequently called "compensation cloud". This screening should be formulated in terms of correlation function. The spin

density of the conduction electron will be denoted by $\vec{\sigma}(r) = \sum_{\alpha\beta} \psi_\alpha^+(r)\,\vec{\sigma}_{\alpha\beta}\,\psi_\beta(r)$ operator if the total spin is

$$\vec{S} + \frac{1}{2}\int \vec{\sigma}(r)\,d^3r \quad . \qquad (4.61)$$

Assuming that the ground state is singlet, thus it is an eigenstate of the total spin operator, it follows that

$$\langle \vec{S}\ (\vec{S} + \tfrac{1}{2}\int \vec{\sigma}(r)\,d^3r)\rangle_{T=0} = 0 \qquad (4.62)$$

thus

$$\langle \vec{S} \int \vec{\sigma}(r)\,d^3r \rangle_{T=0} = -2S(S+1) \qquad (4.63)$$

as $\langle \vec{S}\vec{S}\rangle = S(S+1)$. The energy osscíated with the formtion of the compensation cloud must be in the order of Kondo energy kT_K . This restriction rules immediately out the possibility that the radius of the compensation cloud is in order of the atomic distance, or in other words, localized to the impurity site and to its nearest neighbours, because the energy in question would be then in the order of 1 eV. The other characteristic length which may be anticipated is given by equation (4.28). This quantity is, rather large for small Kondo temperatures, and might be expected to cause measurable effects in different experiments, like NMR and neutron scattering. The actual situation, however, is rather complicated. First of all it would quite obvious to anticipate that in external magnetic field the compensation cloud is polarized in its whole extension, however,it appears that this is not the case . The polarizability at a given distance

can be expressed like

$$\lim_{H\to 0} \frac{\langle \sigma^z(r)\rangle_{T,H}}{H} = \mu_B \langle \sigma^z(r)\,(S^z + \tfrac{1}{2}\int \sigma^z(r')\,d^3r')\rangle \qquad (4.64)$$

where the external magnetic field is in the z-direction. The second form follows from the expansion of the statistical density matrix with respect to H. The polarizability can be split into two terms: (i) conduction electron spin density - impurity spin correlation, $\langle \sigma^z(r) S^z\rangle$ and (ii) conduction electron spin density self-correlation $\frac{1}{2}\langle \sigma^z(r)\int \sigma^z(r)\,d^3r\rangle$.

As we have already seen, the first correlation can not be well localized. The situation is similar for the second term, and to see this let us consider the total spin self-correlation. Assuming again that the ground state is singlet, one obtains for $T=0$ that

$$\langle (\vec{S} + \tfrac{1}{2}\int \vec{\sigma}(r)\,d^3r)^2\rangle = -S(S+1) + \tfrac{1}{2}\langle (\int \vec{\sigma}(r)\,d^3r)^2\rangle \qquad (4.65)$$

where equation (4.63) has been used. As $\langle (\int \vec{\sigma}(r)\,d^3r)^2\rangle = 4S(S+1)$ one may repeat the previous arguments for $\langle \vec{\sigma}(r)\,\vec{S}\rangle$ and thus $\langle \vec{\sigma}(r)\int \vec{\sigma}(r)\,d^3r\rangle$ must be rather extended. In this way the polarizability of the conduction electrons at distance r is the difference of two positive terms, both with large spatial extension. Therefore, one can not decide whether the expression (4.64) is localized inside a few atomic distances or not without a more detailed investigation. Similarly to the situation for other physical quantities however no reliable results are expected for temperatures $T \ll T_K$. In the logarithmic approximation, the behaviour of these two terms can be studied at least at high temperatures.

The most detailed study is due to Müller-Hartmann (1969 and further references can be found there) who used Nagaoka's schema for the Green's function decoupling. This investigation shows the following behaviour.

(i) at low temperatures the correlation becomes strong and independent of the temperature in agreement with our conclusion that this correlation can be expressed only in terms of S.

(ii) $\langle \vec{S}\,\vec{\sigma}(r)\rangle$ constains an oscillating part proportional to r^{3} in the asymptotic region (Rudermann-Kittel-Kasuya-Yoshida like behaviour)

(iii) the terms, $\langle \vec{\sigma}(r)\,\vec{S}\rangle$ and $\langle \vec{\sigma}(r)\,\frac{1}{2}\int \vec{\sigma}(r')\,d^{3}r'\rangle$ have a long range non-oscillating contributions of the form of $r^{-3}\,\frac{S(S+1)}{[\ln(r/\beta T_K)]^{2}}$ but with opposite sign, furthermore, these terms cancel each other in expression (4,64).

Even if this result is reliable only at $T > T_K$, it shows that a complete cancellation in the conduction electron polarization may occur at large distances. This cancellation is very probably quite general and indicates that no longrange behaviour occurs in the non-oscillating polarization caused by the external magnetic field.

As we will see in the next chapter, this idea is supported by the experiments. Looking for the long range behaviour, therefore, the correlations $\langle \vec{\sigma}(r)\,\vec{S}\rangle$ and $\langle \vec{\sigma}(r)\int \vec{\sigma}(r')\,d^{3}r'\rangle$ must be studied directly and only the neutron scattering is an appropriate tool in this respect.

Summarizing these result one may conclude, the compensation cloud has a very large extension, however, only the center part of the spin compensated state can be polarized by external field. Finally, we should mention, that the applicability of the s-d model may be questioned (see section 4.8) with respect to the above problem too and on the other hand no detailed study is known, while starts from the Anderson model.

What must be emphasised, however, is that independently of wheather one uses the s-d or the Anderson model the spin compensation cannot be localized on the d-level only, because it would be associated with a double occupation resulting in a large intraatomic Coulomb energy.

4.11 General remarks

Along chapter 3. we have discussed the structure of d-level density of states $\rho_d(\omega)$. We argued that a broad structure corresponding to the split d-level (broad one-particle resonance of Friedel-Anderson type) must exist, this is indicated in the HF approximation. Futhermore, as a consequence of the singlet ground state and charge neutrality it was suggested in chapter 3., that a narrow resonance must be built up at the Fermi level at T=0, although its dynamical origine was not discussed there. In this chapter we turned to the problem of the Kondo effect which shows up in the form of a resonance at the Fermi level. According to the general relation between the conduction electron scattering amplitude and the density of the d-level, the Abrikosov-Suhl resonance must be superimposed on the broad d-level resonances.

The theory of the Kondo effect was discussed in the s-d model based on the Schrieffer-Wolff trasformation and in that limit of the Anderson model, where the d-level density of states is negligable at the Fermi surface. Thus, the essential assumption of the theories is that the overlap of these two different resonances is small. It is strongly believed that the occurance of the Abrikosov-Suhl resonance does not depend on this assumption, only the mathematical treatment is simplified in that limit.

The general case seems to be too hard for the existing theoretical methods. If one considers the broadening of the d-level first, the treatment of the narrow resonance is extremely difficult thus one start with HF approximation in which the rotational symmertry is broken. The main task would be to restore this symmetry by some mathematical trick which still has not been found. On the other hand, starting with $V_{kd}=0$ and treating this term as a perturbation one cannot arrive at a broad d-level overlapping the Abrikosov-Suhl resonance. It is generally believed that although the mathematical details are not worked out yet, the physical picture is correct.

There are further difficulties in the description of the Abrikosov-Suhl resonance. If one deal with $T \gg T_K$ or $|\omega| \gg kT_K$ there is a mathematical guideline the logarithmic approximation. In the one-particle intermediate state approach this method is extended to lower temperature without further mathematical justification. It is a success of this method that all of the physical quantities remain finite, but it fails to predict the singlet ground state and the correct entropy change. At this point we can state that at low temperature or energy a more general method is required, however, one can be convinced that many of the main features of these results as the monotonically

increasing resistivity and decreasing effective moment with decreasing temperature, bump in the heat capacity around $T=T_K$ are correct. At high temperature the logarithmic behaviour is certainly well justified, however, at low temperature there are not relaible predictions.

A further problem is that the simple s-d model probably results in the unitarity value for the zero-temperature resistivity for all of the spin values S=1/2,1,3/2.. and that contradicts to the charge neutrality. This problem could be cured in a phenomenological way by assuming a small static potential scattering in addition to the exchange interaction, this procedure however seems to be artificial. Therefore, a complete description can be expected only on the basis of the Anderson model.

5. EXPERIMENTS ON DILUTE ALLOYS

5.1 Introduction

Although the phenomenon itself - the resistance minimum and the logarithmic dependence of the resistivity on T - was vell known by experimentalists for about 3o years, a more or less complete experimental situation has emerged only at the end of the sixties.

The main factor for this is that it is often difficult to separate the single impurity properties from interaction effects, these interactions usually have a great influence on the measured parameters. The main sourve of interaction is the RKKY perturbation which provides a long-range indirect coupling between the impurities, and relatively distant impurities can be coupled together. An additional effect, which may be even more important occurs when the impurities are in the Kondo-state. From arguments presented in the previous chapter it follows, that the screening of the impurity spin is performed by electrons in the energy range kT_K around the Fermi level. Therefore, for a free electron band with a bandwidth D, the relative number of conduction electrons which take part in the screening is of the order of kT_K/D and so for an impurity concentration $c_i > kT_K/D$ there are simply no enough conduction electrons for screening. If $T_K \sim 10^\circ K$, then for

$\mathcal{D} = 10\,eV$ this critical concentration is around lo ppm! Naturally this concentration is larger for larger T_K , but then the phenomena connected with the Kondo-effect are weaker, and the separation of the effect due to the impurities from the matrix properties is more difficult.

Local method like Mössbauer-effect (ME), nuclear magnetic resonance (NMR), nuclear orientation (NO) do not suffer from the above limitations, moreover have played an essential,role in this field due to the local character of the problem; other methods like electron spin resonance (ESR) and neutron scattering have not been widely applied and the experiments are not fully understood.

In the following we discuss the experimental situation on alloys which are expected to be appropriate for the Anderson model and use the information obtained mainly on 3d impurities in noble metal or aluminium host. Our goal is to answer the questions raised in the previous chapters, and the experimental fact will be summarized around the following points:

(i) Basic parameters of the Anderson model. Here the HF approximation provides the theoretical background, experiments performed at high temperatures, where many body correlations are absent, are essential in this respect.

(ii) Properties in the Kondo state. The experimental data will be organized to support the assumptions of the previous chapters as well as to demonstrate the consequences of these assumptions. In particular the evidences of the singlet ground state at $T=0$ and the charge neutrality will be discussed. In connection with the experimental facts about the Abrikosov-Suhl resonance and about the correlation effects the question about the validity of the various approximations will be raised as well.

(iii) Relation between the Friedel-Adnerson and the Abrikosov-Suhl resonances. Here we examine the T_K values of various alloys, this provides an experimental test of the Schrieffer-Wolff transformation and of the validity of the s-d model itself.

Finally we attempt to collect those main experimental facts and indications, which still await theoretical explanation; attempts to answer these problems are left to the next chapter where the latest theoretical developments on the Kondo-problem will be discussed.

5.2 Basic parameters of the Anderson model; HF analysis.

In order to gain insight into the nature of the Friedel-Anderson resonances discussed in chapter 2. experiments with energy range comparable with the basic parameters U and Δ are ideal. Macroscopic thermal, transport and magnetic properties give only indirect information on this resonance formation through Fermi surface effects. Local properties are in one hand closely related to the macroscopic properties and therefore reflect low energy processes but in some cases energy distributions well away $\mathcal{E}_F$ are sampled too by these techniques.

Optical experiments are the most important in this context, as the excitation energies involved in the optical absorption process are several eV. In spite of serious limitations considerable impurity concentration around 1 at %, is needed to arrive at a measurable extra absorption, and the class of alloys is limited mainly by the absorption properties of the host etc. these experiments proved to be the most valuable. One expects absorption peak at $E_{d,\sigma}$ with a width somewhat larger than Δ due to the inherent width of the absorption process itself.

Available optical data fully confirm the Friedel-

Anderson picture of the resonance formation in particular the classification of alloys according to the parameter $(U+4\mathcal{F})\rho_d(\varepsilon_F)$. Thus only a single absorption was found in CuNi (Drew and Doezema 1972) well below the Fermi level. The resonance is near Lorentzian, Δ =0,27 eV and E_d=0,75 eV. With these parameters the total number of electrons in the resonance N_d =8,9± o,1, in accordance with the charge neutrality as originally there are 9 electrons in the d-shell of the Ni atom. As the resonance is nearly full $\rho_d(\varepsilon_F)$ is small and therefore this impurity is well in the non-magnetic limit $(U+4\mathcal{F})\rho_d(\varepsilon_F)\ll 1$. In the middle of the 3d series where the density of states is expected to be large well separated absorption peaks appear, these are particularly well pronounced in AgMn (Meyrs et al 1968) and AuMn (Steel and Therene 1971). One resonance is well below the other well above ε_F , $E_{d,\sigma} - E_{d,-\sigma}$ =4,8 eV in these cases this value should be rather near although somewhat smaller than $U+4\mathcal{F}$, see equation (3.2o), Δ = 0,5 eV for both alloys. With these parameters $(U+4\mathcal{F})\rho_d(\varepsilon_F)\sim 3$ therefore both systems are well beyond the HF boundary in the magnetic limit. Other relevant data (for references see Rizzuto 1974 and Grüner 1974) on Au alloys are absorbed in figure 16., where the arrows show the position of the Fermi level with respect the broad resonances the relative positions

of the resonances were inferred from the observed absorption peaks. The precise width of the resonances were not obtained from the experiments we can however assume that Δ is practically constant (of about 0,5 eV), and $U+4\Gamma$ should be reasonable constant too around 5 eV. The virtual bound state seems to be double peaked in these cases except possibly for AuV where the experimental situation is not completely clear, and on the other hand $(U+4\Gamma)\rho_d(\varepsilon_F)\sim 1$ for this alloy. AuNi, however is similar to CuNi, and only one resonance was observed (Drew and Doezema 1973). Similar situation is expected to hold for Ag and Cu alloys, although clear - cut experiments are not available. For Al - alloys optical experiments would be ideal to answer the important question of the parameters which determine the magnetic behaviour. It is expected that Δ is increased compared to noble metal hosts due to the larger density of host states and a reasonalbe factor of two or three increase would result in a "borderline" situation where $(U+4\Gamma)\rho_d(\varepsilon_F)$ is near to one in the middle of the series.

The variation of $\rho_d(\varepsilon_F)$ when moving along the 3d

series and shown in figure 16 is reflected in the high temperature impurity resistivities of these alloys. Figure 17. shows the incremental resistivity R/at % for the alloys in question at room temperature, the double peaked structure, due to the double peaked virtual bound state is evident both for Au and Cu hosts. The HF expression of the resistivity, equation (3.22) describes the main features of the above behaviour and several authors, following Daniel (1962) performed a quantitative analysis using two phase shifts δ_σ and $\delta_{-\sigma}$ coupled together by the Friedel sum rule equation (3.18). Such type of analysis however is not entirely correct, the main objection probably is, that the HF expression neglects the spin-flip scattering, only the potential scattering is retained. The neglection of the spin-flip process might be the most important for Mn impurities, here because of one resonance is well below, the other well above ε_F the potential scattering is fairly small and the impurity represents a well formed spin. In fact, in these cases the resistivity is described reasonable well by the expression, derived from the s-d model

$$R = 2\pi\rho_0 c \left(\frac{\mathcal{J}}{N}\right)^2 S(S+1) \qquad (5.1)$$

with $S = 5/2$ and $\mathcal{J} = 0{,}25$ eV. We shall see later, that

this value $\mathcal{J}$ is in accordance with other estimations.

Although many-body correlations are effective even at room temperature in Al-based alloys, recent high temperature resistivity measurements, shown in figure 18 suggest again in the appearance of a double peaked virtual bound state, at least for Mn, implying that $(u+4\mathcal{J})\rho_d(\varepsilon_F) > 1$ for this case. The separation between the two peaks is probably not so well pronounced than for noble metal hosts due to the larger width Δ

While the resistivity is sensitive to $\rho_d(\varepsilon_F)$ only (see equation 3.22) - and the temperature dependence of R is expected to be small due to the broad (and so weakly energy dependent) d-states (at least in the HF approximation), the thermoelectric power (TEP) reflects the energy derivative of the density of states at ε_F. In the non-magnetic limit of the HF approximation $S = \frac{\pi}{3}\frac{k^2}{e}\frac{T}{\Delta}\sin 2\eta_2(\varepsilon_F)$ however correlation effects should have drastic influence on this parameter. In fact deviations of the measured TEP from that excepted on the basis of the Friedel-Anderson picture with virtual bound state widths derived before signals the strenght of these many-body correlations. Indeed Δ derived from the TEP agrees with that obtained form the optical experiments

only for cases where $(U+4\mathcal{T})\rho_d(\varepsilon_F)$ is small compared to one a classical example is CuNi (Klein and Heeger 1968) $\Delta(TEP)$ evaluated from the low temperature thermoelectric power however decreases drastically as the correlation increases, in CuCo for example it is three times smaller, of about o,15 eV, the situation is similar for AuV. This effect is clearly seen is Al-based alloys, where $\Delta(ETP)$ decreases drastically in the sequence Co, Fe, Mn and then increases again going towards the beginning of the series.

The situation is similar for the specific heat as this parameter is also influenced by low lying fluctuations. The electronic specific heat coefficient

$$\gamma = \frac{3\pi^2}{2} k \rho_d(\varepsilon_F) = \frac{3\pi}{2} k \frac{\sin^2 \frac{N\pi}{10}}{\Delta} \qquad (5.2)$$

in the non-magnetic limit and alloys again to evaulate Δ (see equation 3.42). The drastic reduction of the virtual bound state width evaluated by this way compared to the optical data in Al-based alloys and in AuCo, AuV points again to important correlation effects. Although TEP for magnetic cases like CuMn can be accounted for by a phase-shift analysis similar to that suggested

for the resistivity it is rather hard to estimate the correctness of a such type of analysis. No valuable specific heat experiments were performed on magnetic alloys, mainly due to the fact that impurity interactions are rather important here.

The magnetic properties give the most clear distinction between "magnetic" and "non-magnetic" impurities, although later it will become clear that this distinction is somewhat arbitrary. Not relating the measured temperature dependence of the susceptibility to theoretically derived formulas it is usually accepted that a Curie-Weiss susceptibility

$$\chi(T) = \frac{\mu_{eff}^2}{3k(T+\Theta)} \qquad (5.3)$$

is an indication of a well defined impurity moment, and a Pauli susceptibility shows the absence of the moment. The relation of the above classification to the density ot states is clear (at least in the framework of the Friedel-Anderson picture) a double peaked virtual bound state is connected with a Curie-Weiss, a spin degenerate virtual bound state with a Pauli susceptibility as discussed in section 3.2. This connection is born out from the experiments, Mn, Cr and Fe impurities show a well defined Curie-Weiss behaviour in noble metal hosts, and μ_{eff} decreases going from Mn to Cr and Fe in

$$\rho(H)/\rho(H=0) = 1 - \frac{4 g^2 \mu_B^2 H^2}{27 (kT)^2} \qquad (5.5)$$

(Beal-Monod and Wiener 1969) which explains the experimental findings and gives an estimation of $\frac{\mathcal{J}}{N}$.

The local properties and experiments are essential in dilute alloys a further advantage is that these methods are often free from impurity interaction effects. Until now mainly static properties like local charge and spin distributions have been investigated by ME, NMR and NO techniques, dinamical effects measured by ESR and NMR relaxation experiments and which influence the NO experiments are still not well understood.

Although in a somewhat arbitrary way, but might distinguish between properties measured at the impurity site and at the site of host atoms. In the former case the local susceptibility induces a hiperfine field at the impurity site, resulting in a shift of the NMR line Knight shift and a splitting of the Mössbauer line and has a pronounced effect on the nuclear orientation. This hiperfine field has two contributions coming from the spin adn orbital components of the local susceptibility, the measured field together with the relaxation time can be used to separate of the above two components. The relevant experimental data

It must be mentioned that the first Born approximation of the s-d model is appropriate for describing the properties of strongly magnetic impurities, at least at temperatures $T > T_K$ and then the reduction of the moment from the Hund's rule value $g\sqrt{S(S+1}$ is explained by the antiferromagnetic polarization of the conduction electron states, this polarization is proportional to $\frac{J}{N}\rho_0(\varepsilon_F)$. The total effective moment (see equation 4.5.3)

$$M = g\sqrt{S(S+1)}\left[1 - \frac{J}{N}\rho_0(\varepsilon_F)\right] \quad (5.4)$$

therefore a negative s-d coupling accounts for the observed reduction, see section 4.8.

The most dramatic effect which cannot be understood on the basis of a HF analysis is the giant negative magnetoresistance observed in a number of strongly magnetic alloys (see for example P. Monod 1968), however the s-d model provides a natural explanation of this observation. In the expression of the resistivity (equations 5.1 and 4.10) 2/3 of the csattering amplitude comes from spin-flip, 1/3 from non-spin-flip processes. The spin-flip scattering is frozen out by the application of magnetic field leading to a strong decrease of the resistivity with increasing magnetic field, in small external magnetic fields

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have been summarized by Narath (1972) .

The charge perturbation amplitude, which can be measured by NMR techniques (Bloembergen and Rowland 1953) follows the same pattern as the residual resistivity, available date on Cu-based alloys (Lumpkin 1968 Tompa 1972) indicate a double peaked dependence on the impurity atomic number, similar to figure 17. (Tompa 1972). In Al-based alloys it is single peaked at low temperatures, at high temperatures it becomes double peaked like the impurity resistivity (Grüner and Hargitai 1972 Grüner 1972) .

The measurement of the spin perturbation by NMR method alloys the s-d coupling to be evaluated. This perturbation causes a line broadening, proportional to the external magnetic field, and to the amplitude of the perturbation. This amplitude is proportional to $\frac{J}{N}\rho_0(\varepsilon_F)\chi$ where $\chi = \frac{\langle S^z \rangle}{(J/N)\mu_B H}$. Using the susceptibility data in the same alloys $\frac{J}{N}$ can be derived by a line shape analysis, and relevant experimental data using both data taken on the host and impurity nuclei are shown in figure 19. The overall behaviour, the minimum in the middle of the series is in agreement with the prediction of the Schrieffer-Wolff transformation and will be discussed later.

5.3 The magnetic-nonmagnetic transition: the Kondo effect

The explanation of the resistance minimum, well known by experimentalists for 30 years gave the first indication of a nonperturbative low temperature state at certain cases. Although the above effect has been thought to be a really low temperature phenomenon, it has been suggested later Schrieffer (1967) that T_K may very several decades from alloy to alloy, from the mK region to well above room temperature.

The main features of the magnetic-nonmagnetic transition are well observable although the details may be strongly infuenced by impurity interactions. In the susceptibility θ is a measure of T_k a hump in the thermoelectric power and speific heat as well as a strong increase of the resistivity gives a further indication of the Kondo temperature. These behaviours are displayed is several Review Papers (Van Dam and Van den Berg 1969, Rizzuto 1974) and therfore we list only the arguments for an "experimental scaling" i.e. for the conclusion that the key parameter T_k is the only energy which determines the temperature behaviour of the various physical properties and these properties are rather similar in a reduced T/T_K scale for valious alloys. The most clear-cut

evidence has been supplied by Babic et al (1973) who measured and collected the temperature dependence of the impurity resistivity of various alloys, this plot is shown in figure 2o. While T_K varies from 1 °K (ZnMn) to 5oo °K (AlMn), in all cases $R(T) \sim 1 - \left(\frac{T}{\Theta}\right)^2$ at $T \ll T_k$ then flattens off and becomes logarithmic at $T \gg T_k$ where this temperature range is accessable experimentally. The TEP looks remarkable similar for different alloys too although the sign and magnitude depends on the potential scattering background, this similarity has been first noted by Heeger (1969).

A similar conclusion can be reached by inspecting the temperature dependence of the susceptibilities. In the previous section it has been noted that the susceptibility of AuV has a Pauli form (temperature independent) at low temperatures (with a leading T^2 dependence, van Dam et al 1972) which changes gradually to Curie-Weiss form at higher temperatures. Cu Fe displays a similar behaviour and below 1 °K a susceptibility proportional to T^2 was found although by an indirect way (Triplett and Phillips 197o). In AlMn, where the temperature dependence of χ_{Al} (poor aluminium) makes the evaluation of the contribution from the Mn impurities somewhat ambiguous, the temperature dependence of the impurity Knight shift (Alloul et al 197o) indicates a high temperature

Curie-Weiss behaviour too.

These evidences strongly suggest that the Kondo effect is not restricted to low temperatures but is a more or less common feature of dilute alloys, although the most pronounced effects are found when T_K is small. This suggestion leads to the speculation that some alloys traditionally thought to be nonmagnetic in HF sense are in fact in a Kondo state and a smooth transition between the two types of states exists when $(U+4\Gamma)\rho_d(\varepsilon_F)$ is varied. This continuity hypothesis has not been entirely proved experimentally, various types of experiments like NMK measurements revieved by Narath(1972) point however towards such direction. To reach a final conclusion, however a closer inspection of the properties of the low temperature $T \ll T_K$ Kondo state is required.

5.4 Physical properties in the Kondo state

This section is devoted to the discussion of the nature of the Kondo-state, and that of the magnetic-nonmagnetic transition. Although arguments presented before suggest that the Kondo effect is a rather general phenomenon, here we mainly use experimental information obtained on alloys where clear-cut magnetic behaviour is observed at high temperatures. Thus the nature of the $T \ll T_K$ state is rather different from the high temperature

behaviour in these cases and the effect of Kondo correlations is well observable.

5.4.1 Evidences of a singlet ground state

The susceptibility has been used previdusly to distinguish between magnetic and nonmagnetic impurities, this distinction is based on $\chi(T)$. The Curie-Weiss behaviour can be though to arise from a temperature dependent effective moment thus

$$\chi(T) = \frac{\mu_{eff}^2(T)}{3kT} \quad . \qquad (5.6)$$

The finite susceptibility at $T=0$ shows that μ_{eff} gradually disappears at $T<\Theta$. Using equation (5.6) to interpret the experimental data the temperature dependence of the effective moment can be evaluated. Figure 21 shows $\mu_{eff}(T)$ obtained in this way for AuV alloys (van Dam et al 1972). Although the detailed temperature dependence is slightly different for different V concentrations, for all concentrations $\mu_{eff} \to 0$ as $T \to 0$. This behaviour is reproduced by the temperature dependence of the impurity Knight shift (Narath 1972) , demonstrating that the magnetization disappears at the impurity site and is not due to a negative definite polarization outside

the impurity cell. It must be mentioned, however, that the above findings show only that $\langle S^z \rangle = 0$ at $T=0$ but not S itself, in fact in the Kondo model the latter is constant, see section 4.9 .

The specific heat anomaly, connected with the transition supplies a further evidence for the singlet ground state. The total entropy connected with the transition

$$S = \int_0^\infty \frac{C_v(T)}{T} \, dT \qquad (5.7)$$

can be evaluated from the temperature dependence of the impurity specific heat, for CuCr and CuFe it corresponds to $R \ln(2S+1) = R \ln 4$. (Triplett and Phillips 1970) showing that the high temperature spin disorder entropy has been removed from the system below T_k ie.e the ground state is a singlet.

Although the temperature dependence of the transport properties is not directly related to the singlet nature of the ground state, the strong temperature dependences found in these parameters indicates a strongly temperature and or energy dependent scattering amplitude which builds up at $T < T_k$, the nature of this resonance will be discussed later.

5.4.2 Properties of the Kondo resonance

The question reised at the end of chapter 3.5 must be answered on experimental grounds, this chapter collects various evidences which indicate that a narrow resonance is forming at ε_F in the Kondo state, and analyses the properties of this resonance. These evidences are based partly on macroscopic and partly on local properties, the combination of the two informations is needed to arrive at a firm conclusion. Macroscopic properties - in particular transport properties are essential in this respect - suffer from two limitations:

(i) Being "Fermi surface properties" they are extremely sensitive to small variations of the scattering process near ε_F (in the energy region kT) but give no direct information on the density of states far from the Fermi level.

(ii) Both the energy and temperature dependence of the scattering enters in the relevant expressions of the transport properties. For example the Bethe-Sommerfeld expansion gives for the resistivity

$$R(T) \sim \mathrm{Im}\, t(\varepsilon_F;T) + \frac{\pi^2 k^2 T^2}{6} \left.\frac{\partial^2 \mathrm{Im}\, t(\omega;T)}{\partial \omega^2}\right|_{\omega=\varepsilon_F} \quad (5.8)$$

Therefore both the T and ω dependence influences $R(T)$; the situation is similar for the TEP and Lorentz number, and for the thermal and magnetic properties too.

The local properties often do not suffer from these limitations for example the charge perturbation around the impurities is sensitive to the scattering amplitude far from the Fermi level, and the temperature dependence is driven only by the temperature dependence of the scattering amplitude, see section 4.9, this difference with respect the resistivity will be used later to seperate the energy and temperature dependences.

The scattering amplitude at $T=0$ however is not influenced by the many body effects which lead to strong energy dependences, and is determined only by the total number of electrons introduced by the impurity, (equation 3.41) is independent of the approximations involved and has a general validity. Figure 22. shows the impurity resistivities extrapolated to $T=0$ for Cu, Au and Al based alloys, for CuMn, CuCr and AuMn the Kondo temperature is so low that no relevant experiments exist below T_K. The full line is calculated using equation (3.41). The good agreement between the calculated and measured points

provides a firm basis of the charge neutrality. A further piece of evidence can be given by comparing $\Delta R = R(T \ll T_k) - R(T \gg T_k)$ for CuFe and CuCr. As the high temperature spins of the two impurities are nearly identical ΔR should be the same for the two impurities, if it is proportional to S as suggested (Schrieffer 1967) while for the charge neutrality to hold it should be given by the difference of the high $(T \gg T_k)$ and low $(T \ll T_k)$ temperature expressions of $R(T)$, (equations 3.22 and 3.41), this difference is shown in figure 21. too. Experimental values of ΔR are $20\,\mu\Omega\,cm/at\%$ for Cr and $8\,\mu\Omega/at\%$ for Fe impurities clearly favouring the picture we have presented on the basis of the charge neutrality in section 3.6. Charge perturbation amplitudes for Al-based alloys extrapolated to $T = 0$ are also in agreement with the charge neutrality condition, and the oscillation amplitudes can well be described by equation (4.54) with one phase shift which is independent of the spin direction.

We stress again, that although equation (3.41) is the same than that obtained on the basis of the HF approximation in the nonmagnetic limit, it has a more general validity and does not require a simple Lorantzian density of states.

The energy dependence of the density of states enters into the expression of the temperature dependences of the transport properties, although it is mixed together with the temperature dependence of $\rho_d(\varepsilon_F)$. Therefore the question about the density of states raised in chapter 3.5 cannot be resolved by inspecting the transport properties alone. Comparing however these temperature dependences with that of a related local property the charge perturbation around the impurities, the energy and temperature dependence can be separated. The reason is that while the low temperature resistivity is given by equation (5.8) and two terms contribute to the temperature dependence, the charge oscillation amplitude reflects only $t(\varepsilon_F;T)$ therefore by comparing equations ([redacted]) , $\frac{\partial^2 t(\omega)}{\partial \omega^2}$ can be evaluated in certain cases (Grüner and Hargitai 1971) . Such analysis leads to a strongly energy dependent scattering amplitude near ε_F for AlMn, this can be characterized by a width of about 0.1eV which is near to kT_K for this alloy. It supports therefore possibility (ii) in section 3.5 i.e. that a sharp resonance is built up at ε_F . This is the Abrokosov-Suhl resonance, discussed in section 4.

As the resonance has a width approximately kT_k, both the low and high energy parts of this resonance can be studied if the temperature range of the experiments extends from well below to well above the Kondo temperature.

Theoretical formulas obtained on the basis of the s-d model cover the whole temperature interval in question and can be compared with the experimental findings. Such a comparision is presented in figure 22., where $R(T)$ measured in $Cu_x Au_{1-x} Fe$ alloys is compared with the Hamman curve equation (4.38). The full line is calculated by adjusting S to achieve good agreement with the experiments, this gives $S = 0.77$ (this is much smaller than the spin 3/2 observed in the susceptibility). The agreement is poor expecially at low temperatures, where $R(T) \sim 1 - (T/\theta)^2$ experimentally, while $\frac{\partial R(T)}{\partial T}$ diverges in Hamman's expression. This disagreement, which holds for the other transport and for the termal and magnetic properties, is however not fundamental as far as the model is concerned, but is probably due to the approximations involved, the above analysis

shows that they break down going below T_K . The situation is even worse for the ground-state models, where drastic deviations from experiments were found (Star et at 1972) , the good agreement claimed by Heeger (1969)is caused by impurity interaction effects.

In this situation one mus abandon the hope for a perfect agreement between theory and experiment and it is more useful to inspect the temperature regions where the physical properties are determined by the same temperature dependences, even though the origin of these dependences is not fully understood. Two temperature regions are ~~of these~~ essential in this respect: the $T \gg T_K$ and $T \ll T_K$ behaviours of the various alloys. The s-d model as a firm theoretical background where the formulas are expected to work can be used only to account for the $T \gg T_K$ properties, for $T \ll T_K$ we use the assumption of a simple single particle like resonance to arrive at a common physical picture.

The high energy behaviours are controlled by logarithmic dependences, the most famous of them is the logarithmic increase of the resisitivity with decreasing temperature. Clear-cut logarithmic behaviours are expected

however only at $T \gg T_k$ the successive leading logarithmic terms are important even at temperatures one or two orders of magnitude larger than T_k . This feature of the logarithmic approximation provides merely a warning towards ecperimentalists, that only alloys with very low T_k are suitable for a straight comparision with perturbational expressions, and strictly speaking only alloys of noble metals with Mn impurities (where T_k is much less than 1 ^{o}K) are suitable in this respect. Indeed, logarithmic temperature dependences over broad temperature intervals were found only in these cases, and equation (4.19) fits the experimental results with reasonable coupling constants. No such analysis is appropriate for other cases where T_K is larger than 1 ^{o}K. The Curie-Weiss behaviour of the susceptibility is in fact also in agreement with perturbational expressions based on the s-d model. Equation (4.27) can be approximated with a Curie-Weiss form over a broad temperature interval, with $\mu_{eff} = g\sqrt{S(S+1)}/1.22$ and $\theta = 4.5\, T_K$, T_k is given by equation (4.26) Therefore the high temperature susceptibilities of "magnetic" impurities discussed in section 5.2 are in

agreement with a logarithmic behaviour af this parameter. No valuable specific heat experiments related to this question are available.

The overall behaviour of the $T \ll T_K$ properties is completely different from the high temperature logarithmic dependences, and by now it is generally accepted that the low energy processes are controlled by simple power laws on the temperature. Furthermore, the temperature dependences of the various physical parameters are ~~the~~ similar to ~~same~~ as for an interacting Fermi gas, i.e.

This has been first demonstrated by Caplin and Rizzuto (1968) on AlMn

$$R(T) = R(0)\left[1 - \left(T/\theta_R\right)^2\right] \quad \text{resistivity}$$

$$C_V(T) = \frac{T}{\theta}\left[1 - \left(T/\theta_c\right)^2\right] \quad \text{specific heat} \qquad (5.8)$$

$$\chi(T) = \chi_0\left[1 - \left(T/\theta_\chi\right)^2\right] \quad \text{susceptibility}$$

where the θ values may be somewhat different because $\rho_d(\omega)$ is temperature dependent too.

The TEP is a liner function of the temperature, the magnitude is determined by the potential scattering background too. This behaviour of the transport, thermal and magnetic properties is well confirmed experimentally, in particular in CuFe ($\theta \sim 20°K$) AuV ($\theta \sim 300°K$) and AlMn ($\theta \sim 10^3 °K$). The characteristic temperatures are of the same order of magnitude, than the temperature

where the magnetic nonmagnetic transition occurs at least for the first two cases thus giving evidence that the transition temperature and the width of the many body resonance are strongly correlated.

This change of regime from logarithmic to simple power laws is the basic unresolved question in this field, this contrasting behaviour at $T \gg T_K$ and $T \ll T_K$ has generated the family of more sophisticated theoretical techniques to attack the s-d model, these techniques will be discussed in chapter 6.

5.4.3 Correlation effects in the Kondo state

As the Kondo type screening of the impurity spin is a long range correlation effect, with a characteristic distance $\xi_K = \frac{v_F}{kT_K}$ the nature of the Kondo state should be manifested in anomalous charge and spin perturbations around the impurity within this distance as discussed in sections 4.8 and 4.1o. For an impurity with $T_K \sim 10^\circ K$ this distance is of about 10^3 Å therefore this correlation effect should be well observable by studying the properties of the host by local methods. NMR is well suited for a such type of investigation and indeed

both the charge and spin perturbations were investigated with this technique.

The radial depencence of the charge perturbation has been fully investigated in Al-3d transition metal alloys, this perturbation is reflected through the quadrupole effects on the NMR signal. As discussed in Chapter 4.9 a strong depression of the charge perturbation is expected within the characteristic distance $\xi_{\delta\omega}$ when compared with the assymptotic Friedel expression, figure 23. shows the radial dependence of the charge perturbation around Cr and Mn impurities in aluminium, the strong depression of $\Delta\rho(r)$ is evident in both cases. A comparision (Berthier and Minier 1973) with the theory discussed in section 4.9. gives a characteristic distance $\xi \sim 10\mathring{A}$ and thus an average width $\Gamma \sim 0.5\,eV$ of the scattering amplitude. The significance of this result becomes clear, when compared with other estimations of the width of the resonances

(i) It is definitely smaller than the single particle width Δ which is at least 1 eV for Al based alloys.

(ii) Γ is much larger than the effetive width, Δ' determined from the comparasition of the temperature dependence of the charge perturbation and resistivity (see section 5.4.2).

The dilemma can be resolved only by assuming that the resonance has a sharp top at $\mathcal{E}_F$ this is reflected by the small Δ' however has long tails, therefore the average energy dependence sampled by the preasymptotic behaviour is weaker. This behaviour is in full agreement with the representation of figure 22/b and supplies the basic evidence, that the resonance in the Kondo state consists of both the broad single-particle (Friedel-Anderson) and narrow many-body (Suhl-Abrikosov resonances).

The behaviour of the spatial distribution of the magnetization has been thoroughfully investigated in CuFe by various techniques, and various interpretations appeared from time to time to account for the observed anomalies. The experimental information has been supplied by three techniques: macroscopic susceptibility, ME on the iron impurities and host NMR measurements. Impurity interaction effects have a dominant role in this system, and the contribution of the single impurities to the measured behaviour has been separated only recently. The experimental findigns can be summarized as follows:

(i) The magroscopic susceptibility is given by a Curie-Weiss law down to 1 ^{o}K where is flattens off and can be represented by a $1-\left(\frac{T}{\Theta}\right)^2$ dependence (Thoulouse and Tournier 1969, Triplett and Phillips 1970) .

into a temperature dependent s-d coupling although this suggestion needs a confirmation from theoretical side. The spatial distribution of the polarization however may be rather different from the correlation function $\langle \vec{S}\ \vec{\sigma}(r) \rangle$, which is expected to have a spatial distribution drastically different from the polarization. Unfortunately recent efforts to measure the correlation function itself by diffuse neutron scattering were not entisely succesful (Kroó and Szentirmay 1972, Bauer and Seitz 1972)

By concluding it appears that the Kondo correlation effect influences the behaviour of the charge perturbation around the impurities but does not affect the polarization itself. This duality - although being partially resolved by the classical approaches of the Kondo effect discussed in chapter 4 - still awaits a theoretical clarification.

5.5 Relation between the single particle and many-body resonances.

Both the single particle (Friedel-Anderson) and many-body resonances of Abrikosov-Suhl type are well confirmed experimentally, however no relation has been demonstrated to exsist between these two types of resonances. Intuitively it is clear that a large single particle

into a temperature dependent s-d coupling although this suggestion needs a confirmation from theoretical side. The spatial distribution of the polarization however may be rather different from the correlation function $\langle \vec{S}\ \vec{\sigma}(r) \rangle$, which is expected to have a spatial distribution drastically different from the polarization. Unfortunately recent efforts to measure the correlation function itself by diffuse neutron scattering were not entisely succesful (Kroó and Szentirmay 1972, Bauer and Seitz 1972)

By concluding it appears that the Kondo correlation effect influences the behaviour of the charge perturbation around the impurities but does not affect the polarization itself. This duality - although being partially resolved by the classical approaches of the Kondo effect discussed in chapter 4 - still awaits a theoretical clarification.

5.5 Relation between the single particle and many-body resonances.

Both the single particle (Friedel-Anderson) and many-body resonances of Abrikosov-Suhl type are well confirmed experimentally, however no relation has been demonstrated to exsist between these two types of resonances. Intuitively it is clear that a large single particle

density of states near ε_F means that the many-body resonance, which should reach the charge neutrality limit at $T=0$ can be built up more easily, thus it is width proportional to T_K is larger. Looking at figure 16, T_K shuld have a minimum is the middle of the series. The dependence of T_K on the impurity atomic number is shown in figure 25 (see for example Heeger 1969, Grüner 1974) for Au and Cu based alloys. The four orders of magnitude change of T_K suggests a rather drastic dependence of the Kondo temperature on $(U+4\Gamma)\,\rho_d(\varepsilon_F)$ . . The connection between figure 25 and 16 can be further seen in figure 19, and then T_K has a rather strong dependence on $\mathcal{J}/N$.

Even the non-degenerate Anderson model can explain this behaviour at least in a certain range of the parameters of the model. Namely the Schrieffer-Wolff transformation (equation 4.49) connects $\frac{\mathcal{J}}{N}$ to the Anderson parameters U and Δ and describes the behaviour of T_K when going through the 3d series, and then the expression of the Kondo temperature accounts for the widespread T_K values. Although the Schrieffer-Wolff transformation works only for strongly magnetic cases, the inclusion of nonresonant (potential scattering) phase shifts into the s-d model could be in principle used to extend the relation between the Anderson and s-d models.

It should be mentioned that orbital degeneracy certainly plays an important role here, in fact the extension of the Schrieffer-Wolff transformation to orbitally degenerate impurities shows that $\frac{T}{N} \sim \frac{1}{S}$ and than the application of Hund's rule explains the V shaped behaviour of $\frac{T}{N}$ versus the impurity atomic number (Daybell and Steyert 1968). This explanation however requires the Schrieffer-Wolff transformation to hold for cases other than Mn too and we have seen previously that this hypothesis is confirmed neither experimentally, nor theoretically.

In the light of the restricted validity of the Schrieffer-Wolff transformation the question about the validity of the s-d model itself has to be reised again. The model certainly works for strongly magnetic cases like CuMn, we believe however that the main features of the physics behind the s-d model survives also for intermeditate situations like AlMn and goes over progressively to a HF nonmagnetic state with decreasing $(u+4\mathcal{T})\rho_d(\varepsilon_F)$. The smooth transition from a spin-compensated ground state to a nonmagnetic state in HF sense can be visualized in the following way: the resonance in the Kondo state consists of two well separated Friedel-Anderson resonances andna narrow Abrikosov-Suhl resonance. With decreasing $(u+4\mathcal{T})\rho_d(\varepsilon_F)$ the Friedel-Anderson resonances move closer

to each other, while the width of the Abrikosov-Suhl resonance increases rapidly. The distinction between the two types of resonances is progressively smeared out, and finally for $(u+4\mathcal{J})\rho_d(\varepsilon_F) \ll 1$, the resonance looks like a single Lorentzian. This transition is smooth as it is similar to the magnetic-nonmagnetic transition as a function of temperature. This transition may be in fact described with an s-d coupling sonstant which increases from the Schrieffer-Wolff value to an unitarity limit as $(u+4\mathcal{J})\rho_d(\varepsilon_F)$ goes to zero. On experimental grounds it seems that this value is given by $\frac{\mathcal{J}}{N}\rho_0(\varepsilon_F) = 1$ (see for example Narath 1972), this suggestion however has not been confirmed yet theoretically.

6. RECENT THEORETICAL DEVELOPEMENTS: INFRARED DIVERGENCIES AND SCALING LAWS

As we have discussed in the previous chapters the theoretical problemsto be solved are the low temperature behaviour in the s-d model and a unified theory describing simultaneuosly the narrow and broad resonances within the Anderson model. In the last few years considerable progress was achieved in the first field realizing the importance of infrared divergencies and scaling laws. This will be discussed along the main part of the present chapter. The second problem has been proved to be more difficult, and the functional integral approach of the Anderson model was hampered by mathematical difficulties, some remarks on this approach will be given in section 6.6.

6.1 Many particles in the intermediate states

Abrikosov's theory where only the leading logarithmic terms are considered breaks down as the Kondo temperature T_K is approached form high temperatures. As it has been pointed out at the end of section 4.3, there are two drawbacks in the leading logarithmic approximation: omission of all the imaginary parts and the restriction to certain class of diagrams (the parquet diagrams).

The one particle intermediate state approximation reviewed in section 4.4 suffers however, only form the second simplification. As it was shown along the chapter 4, this theory of the Abrikosov-Suhl resonance is still sutisfactory except in regions $T \gg T_K$ or $|\omega| \gg T_K$, and is in contradiction with experimental findings, see chapter 5. The main part of thie chapter is devoted to those theories which were constructed to go beyond the one particle intermediate state approximation.

The milestone of this line is Anderson's work (1967/b) where the Kondo problem is related to infrared divergencies which have already been a well-known phenomena in qunatum field theory. Namely, a finite energy loss of a particle may be associated with a creation of a very large or even infinite number of exciations if the energy spectrum of these exciations starts at zero energy. In the Kondo problem the relevant excitations are electron-hole pairs with small energy. The production of a large number of these excitations leads to the importance of the many particle intermediate states.

We discuss first the problem of infrared divergencies and then its application to the Kondo effect.
The investigation of the latter problem was started using different approaches:

(i) Anderson et al outlined a scaling theory for thermodynamical quantities in a series os papers (Yuval and Anderson 1970, Anderson Yuval and Hamann 1970/a, 1970/b and Anderson and Yuval 1971) and the Kondo problem was related to one-dimensional models. This approach will be discussed in section 6.3.

(ii) Using the diagram representation Fazekas and Zawadowski (1969) demonstrated that one has to go beyond the "parquet" approximation, futhermore, Maleev (1969) included electron-hole pairs in his dispersion theory. This line to discussed in section 4.4 has been developed by making use of dynamical renormalization group (Zawadowski and Fowler 1970 and Abrikosov and Migdal 1970)

(iii) Wilson's recent contribution to the phase transition theory (see Wilson-Kohut 1973) which is based on renormalization group was followed by a numerical treatment of the Kondo effect with great sucsess. We discuss this approach in section 6.5.

6.2 Infrared divergencies

In order to demonstrate the origin of the infrared divergencies occuring in differnt physical problems Anderson (1967/b) considered a very simple case of a noninteracting electron gas in a well localized impurity potential V (see Hamiltonian 4.6) and

thereafter he compared the ground states corresponding to the cases $V \neq 0$ and $V=0$. The instructive conclusion was that these two ground states have only a small overlap which goes to zero as $\Omega^{-\varepsilon}$ ($\varepsilon > 0$) if the volume of the electron gas tends to infinite. Thus in case $\Omega = \infty$ the ground states are orthogonal to each other. This orthogonality is due to the fact that the ground state with potential can be expressed in terms of the unperturbed free electron states and the electron-hole pair excitations occur with large relative amplitudes, because these pairs can be excited with arbitrary small energies. One may conclude, that if a localized potential is suddenly changed then in the rearrangement of the electron gas an infinite number of electron-hole pairs are involved. The infrared divergencies has been presented by Hopefield (1969) in a simple manner.

Mahan (1967) has proposed a simple physical problem where this phenomenon results in measurable quantities, this is the X-ray absorbtion. In a metal the X-ray absorbtion problem means that a deeply lying electron of an atom is excited by X-ray into the continuum above the Fermi level. The potential representing the atom is changed and due to this process a new arrengement in the electron gas is set up to screen this potential. The time-dependence of the rearrengement is reflected in the X-ray absorbtion spectrum near the threshold and shows a particular asymptotic behavious, namely, the remainder of the old arrengement dies out

according to some power function $1/t^{\alpha}$ instead of the exponential $e^{-\alpha' t}$ expected in general.

The theoretical formulation of this problem has a strong resamblance to the Abrikosov's pseudofermion representation of the impurity spin in the Kondo problem (see section 4.3) the deeply lying electron corresponds to the pseudofermion but withour (2S+1)-fold spin degeneracy, and the interaction between the deeply lying electron and the conduction electron is spin independent. Nozières et al (Roulet et al 1969 and Nozières et al 1969) developed a theory based on diagram technique where not only the leading logarithmic but the next leading terms are considered too. Starting from the perturbation theory the vertex corrections due to parquet diagrams cancel each other as it has already been demonstrated in section 4.2 for the scattering amplitude in the second order. Moreover, additional vertex and self-energy corrections occur in third order of the perturbation theory, these diagrams are shown in figure 26. These diagrams give the skeletons for Nozières's self-consistant theory. It is important to mention that in the X-ray problem the vertex and self-energy corrections cancel each other again due to an exact identity of Ward-type, thus the strength of the scattering is not enhanced, as it does for resonant scattering. In order to demonstrate the typical analytical functioanal forms achieved in the X-ray absorbtion problem we refer to the deep electron

Green's function which is given by (Nozières et al)

$$G(\omega) = -\frac{1}{\omega}\left(\frac{\omega}{D}\right)^{g^2} \qquad (6.1)$$

where ω is the energy measured from the absorbtion edge, the coupling g is proportional to the potential change, D is the width of the conduction band. The corredtion to the free propagator $G^{(0)}(\omega) = -\frac{1}{\omega}$ $(g=0)$ shows up as a result of summation of typical logarithmic terms, namely,

$$\left(\frac{\omega}{D}\right)^{g^2} = e^{g^2 \ln\left(\frac{\omega}{D}\right)} = \sum_{n=0}^{\infty} \frac{1}{n!} g^{2n} \ln^n\left(\frac{\omega}{D}\right). \qquad (6.2)$$

This formula demonstrates how the summation of logarithmic terms results in simple power behaviour.

A more detailed study of the question given by Nozières and De Domonicis (1969) shows that the X-ray absorbtion is actually a one-body problem where the non-interacting electrons move in a time-dependent potential associated with the excitation of the deep electron and this becomes obvious in time-dependent representation but is not trivial in energy repesentation. In this problem no resonance occurs. The time-dependent problem was solved exactly by Nozieres and De Dominicis and the result obtained are similar to those derived by perturbation theory if the coupling is replaced by δ/π, where the phase shift δ corresponds to the scattering on the potential change. The response function of the X-ray absorbtion was derived which is exact in the

asymptotic region with respect the time variable and the correction term due to the potential change can be written as

$$(iDt)^{2\frac{\delta}{\pi}-\frac{\delta^2}{\pi^2}} \quad . \qquad (6.3)$$

This exhibits again the typical power behaviour. This correction, however, is asymptotical, because at small times $t \sim 1/D$ the shape of the conduction band has an important role and this cut-off problem was not treated in an oversimplified way. Finally, we mention, that for strong coupling the diagram technique breaks down because further classes of diagrams enters into the problem and already the"envelope" diagram shown in figure 27 is not included, thus the extension of the theory in a digrammatic way seems to be too complicated.

6.3 Thermodynamical scaling

Anderson and Yuval (Yuval and Anderson 197o and Anderson, Yuval and Hamann 197o/a) called the attention to the importance of the infrared divergencies in the Kondo effect arguing in the following way. First of all an anisotropic Kondo model was introduced where the two terms in the Hamiltonian (4,4) have different amplitudes, thus

$$H_1 = H_z + H_{\pm} \tag{6.4}$$

where

$$H_z = -J_z \sum_{kk'} S^z \left(a^+_{k'\uparrow} a_{k\uparrow} - a^+_{k'\downarrow} a_{k\downarrow}\right) \tag{6.5}$$

$$H_{\pm} = -J_{\pm} \sum_{kk'} \left\{S^+ a^+_{k'\downarrow} a_{k\uparrow} + S^- a^+_{k'\uparrow} a_{k\downarrow}\right\} \tag{6.6}$$

whith coupling constants J_z and $J_{\pm}$ for the spin conserving and spin-flip terms, respectively. (In Anderson's works the coupling constants introduced are different by the factor -2). If the z-component of the spin is fixed then H_z has an effect on the electron gas like a spin-dependent static impurity potential. The spin-flip due to $H_{\pm}$ is associated with a sudden change of the potential. Therefore, one spin-flip corresponds to the problem discussed by Nozieres and De Dominicis (1969) in connection with the X-ray absorption. Their exact asymptotic solution can be directly applied. In the Kondo problem, however, there is a sequence of spin-flip processes, and the necessary generalization was given by Yuval and Anderson (197o) in a very elegant mathematical form working with determinants built up from time dependent Green's

functions. They succeeded to give the partition function in a closed form by evaluating those determinants. The result can be written as

$$\overline{Tr\left\{\exp(-\beta H)\right\}} = \sum_{n=0}^{\infty} J_{\pm}^{2n} \int_0^{\beta} d\beta_{2n} \int_0^{\beta_{2n}-\tau} d\beta_{2n-1} \times \cdots \int_0^{\beta_2-\tau} d\beta_1 \exp\left\{\sum_{i>j} (-1)^{i-j} (2-\varepsilon) \ln \frac{\beta_i-\beta_j}{\tau}\right\} \tag{6.7}$$

with

$$\varepsilon = 8\,\frac{\delta_{\uparrow\downarrow}-\delta_{\uparrow\uparrow}}{\pi} - 2\left(\frac{\delta_{\uparrow\downarrow}-\delta_{\uparrow\uparrow}}{\pi}\right)^2 \tag{6.8}$$

where $\delta_{\uparrow\uparrow}$ and $\delta_{\uparrow\downarrow}$ are the conduction electron phase shifts in the cases where the conduction electron spin is parallel and antiparallel to the impurity spin and $\delta_{\uparrow\downarrow}$ and $\delta_{\uparrow\uparrow}$ depend only on J_z . The partition function is given as a product of integrals. As we have already mentioned at the end of the previous section, the solution given by Nozieres and De Dominicis breaks down at short time $\tau \sim D^{-1}$ because of the approximate cut-off procedure applied. In order to avoid this difficulty time intervals proceeding the spin-flips are eliminated by modifying the upper limits of the integrals. The approximate nature of this procedure does not lead to any serious problem as far as the total length of these spurious intervals is negligible compared to the total path of the integrals thus the spin-flips are not too frequent. Studying of the form of the partition function given by equation (6.7) Anderson and Yuval realized that this partition function corresponds to a classical problem at the same time.

In this classical problem a line of length β is divided into rods alternatively charged with positive and negative signs. The interaction between the charges shows logarithmic dependence on the distance as $(-1)^{i-j} \ln \frac{|\beta_i - \beta_j|}{\tau}$ and the strength of the interaction is given by $(2-\varepsilon)$ The "chemical potential" for the boundary points is proportional to the spin-flip amlitude $J_{\pm}$ standing in front of the integrals. Although the classical problem looks very simple, this partition function can not be exactly treated. It is interesting to note, that by transforming the integrals into sums a one-dimensional Ising problem is achieved (Anderson and Yuval 1971) with long-range interaction of type $1/r^2$ associated with next neighbour interaction as well which has interest on its own right.

In order to study this partition function Anderson and Yuval turned to the scaling with respect to the conduction electron band width i.e. the inverse of the short time cut off $\tilde{\tau}^{-1}$. The idea is to change $\tilde{\tau}$ by $d\tilde{\tau}$ and afterwards to modify the coupling strengths $J_{\pm}$ and ε in such a way that the partition function remains invariant. This program was worked out and it can be presented in a very simple way (see Anderson, Yuval and Hamann 1970/b), however here we restrict ourselves to the discussion of the scalling properties, which are given by the following scalling equations

$$d\varepsilon = \left[(2-\varepsilon)^2/(2-\varepsilon_0)\right](2J_{\pm}\tau)^2 \frac{d\tau}{\tau} \qquad (6.9)$$

$$d \ln (J_{\pm}^2 \tau^2) = \varepsilon \frac{d\tau}{\tau} \qquad (6.10)$$

where in the weak coupling limit $\varepsilon = 4\mathcal{J}_z\tau$ and $\varepsilon_0^2 = \varepsilon^2 - (4\mathcal{J}_\pm\tau)^2$ is an invariant quantity under the scaling. The scaling curves are shown in figure 28. with arrows indicating the direction of increasing τ . The isotropic case scales along the straight lines, and for ferromagnetic coupling the scaling shows toward the weak coupling limit, in the antiferromagnetic case however toward the strong coupling regime.

The scaling curves below the straight lines connect an Ising type model ($\mathcal{J}_\pm = 0$) with the anisotropic Kondo problem. The Anderson-Yuval scaling is exact in the weak coupling limit but with increasing coupling strength the spin-flip processes become dense in expression 6.7 and more accurate treatment of the cut-off may be required as it was emphasized by Anderson, Yuval and Hamann (1970/a). This problem will be discussed in section 6.7 in connection with the value of the Kondo temperature.

The most important consequence of this scaling theory is that the coupling strength becomes infinite along the antiferromagnetic scaling lines. The argument is based on the fact that the problem is related to one-dimensional problems in which there should not be any singular behaviour at finite coupling, thus there is no singular point on the scaling plane in which the curves may end, thus they go to infinity (see e.g. Anderson 1972 and Fowler 1972) . This relies on the plausible assumption that the connection

between the Kondo problem and one-dimensional systems holds even in the strong coupling limit.

Finally, we should mention that studying the special case of $\varepsilon=1$ Toulouse (1969) realized that this limit is exactly solvable. This "Toulouse limit" can be represented by a vertical line on the antiferromagnetic side of the scaling plane somewhere in the medium strong coupling regime of J_z. It is believed that the scaling into the "Toulouse limit" may be a key to solve the Kondo problem, numerical predictions however have not yet been obtained in that way. The situation becomes more complicated by the fact, that it is not clear how accurate the expression 6.7 itself is in the strong coupling limit (cut-off procedure).

Emery and Luther (1971) worked out a theory which is in many sences similar to those discussed above, however, there are smaller discrepancies as well. They transformed the problem in another one, where the spin is interacting with a Boson field and the treatment is based on the long time approximation introduced by Nozières and de Dominicis (1969).

ratures like in the X-ray absorption problem (see e.g. equation 6.1) and a power dependence is left. The Nozieres method has been applied by several other authors among them Murata (1971) and Fukushima (1971) to the Kondo problem. It is worth mentioning that these theories provide a T^2 — dependence for the low temperature resistivity, but this square form is rather dubious because it relies entirely on the self-consistent parquet approximation which breaks down there. To include the imaginary parts, as well, seems to be a rather hopeless problem at least in this theory.

To sum up a certain class of diagrams in logarithmic problems the renormalization group method is very adequate (Bogoliubov and Shirkov 1959) and it may lead to scalings. On the other hand, Anderson (1970) has suggested a very simple scaling idea. First, because of its simplicity, this elementary scaling will be presented in a form generalized by Sólyom and Zawadowski (1973) to make it capable of taking into account many particle intermediate states.

The conduction electron scattering amplitude is considered in Schrödinger perturbation theory, and the amplitude is normalized according to the norm of the initial and final states $|i\rangle$ and $|f\rangle$ with momenta k and k' being near to the Fermi surface. This normalized scattering amplitude is

$$T(\omega/D; J_{\pm}, J_z) = \frac{\langle f| \sum_{n=0}^{\infty} H_1 \left(\frac{1}{\omega - H_0} H_1\right)^n |i\rangle}{\sqrt{\langle f| \sum_{n=0}^{\infty} \left(\frac{1}{\omega - H_0} H_1\right)^n |f\rangle \langle i| \sum_{n=0}^{\infty} \left(\frac{1}{\omega - H_0} H_1\right)^n |i\rangle}} \quad (6.12)$$

This quantity is closely related to the effective coupling given by equation (6.11) . The scaling idea for a fixed energy ω can be formulated as to change the conduction electron band width and the coupling constants by ΔD and $\Delta J_{\pm}$, ΔJ_z respectively, in such a way that the normalized scattering amplitude remain invariant, thus

$$\frac{\partial T(\omega/D; J_{\pm}, J_z)}{\partial D}\Delta D + \frac{\partial T(\omega/D; J_{\pm}, J_z)}{\partial J_{\pm}}\Delta J_{\pm} + \frac{\partial T(\omega/D; J_{\pm}, J_z)}{\partial J_z}\Delta J_z = 0 \qquad (6.13)$$

These equations (one in the isotropic and two in the anisotropic case) establish the scaling. If the derivatives are known, effective ω/D dependent coupling constants can be defined as the solutions of this equation, which agree for $J_{\pm}=J_{-}$ with the one introduced by equation (6.11) . These derivatives are calculated in Schrödinger perturbation theory. The first order scaling is achieved by calculating the numerator of expression (6.12) up to the second order and the effective coupling obtained is equivalent with the spin-flip scattering amplitude in Abrikosov's theory, furthermore, in the weak coupling limit with that derived in the Anderson-Yuval theory. In the second order scaling the numerator is calculated up to third order and the denominator up to second thus the diagrams in figure 27. are included as well. The differential equation obtained e.g. for the isotropic case is

$$\frac{\partial}{\partial \ln \frac{D}{\omega}} J_{eff}\left(\frac{\omega}{D}\right) = -\left[J_{eff}\left(\frac{\omega}{D}\right) - \frac{1}{2} J^2_{eff}\left(\frac{\omega}{D}\right)\right] \qquad (6.14)$$

and the solution of this equation remains finite in the whole energy interval as it is shown by figure 29., furthermore, its behaviour is smoother than the Abrikosov's first-order scaling in agreement with the expectation discussed at the beginning of the present section.

The scaling idea can be summarized in such a way that the problem with large $\ln(\omega/D)$ and small J is equivalent with another one where $\ln(\omega/D)$ is not so large but J becomes larger. The scaling can be formulated in terms of energy and cut-off as well and the temperature dependence is similar to the energy dependence. As the summation of diagrams (e.g. the self-consistent parquet approximation), the dynamical scaling also breaks down at large effective coupling thus at small energy and low temperature since the coefficients of equation (6.13) are calculated by using perturbation theory. It may be mentioned that in anisotropic case there is a singular point on the antiferromagnetic side of the scaling plane where all of the scaling curves run in. The existance of such singular point is rather dubious, see discussion at the end of section 6.3. Furthermore, by solving equation (6.14) for small energies it can be demonstrated that the logarithmic behaviour is changed to power T^2 and ω^2 dependence at $\omega = 0$ and $T = 0$, but the square dependence is again doubtful.

Historically, the second order scaling has been first

derived on the basis of renormalization group by Zawadowski and Fowler (197o) and Abrikosov and Migdal (197o) , which method has been suggested by Gell-Mann and Low (see Bogoliubov and Shirkov 1959) and it has been proved to be very adaquate in case of logarithmic problems where scaling occurs (for a review see Zawadowski 1973). The main idea is as follows. The quantities in a Green's function theory as the vertex $\Gamma(\omega)$ pseudofermion and electron Green's functions, $G_J(\omega)$ and $G_I(\omega)$ respectively, furthermore the coupling constant J are multiplied by arbitrary constant factors Z_1, Z_2 and Z_3 in the following way

$$G_J \to z_1 G_J \;,\; G_I \to z_2 G_I \;,\; \Gamma \to z_3^{-1}\Gamma \text{ and } J \to z_3 z_1^{-1} z_2^{-1} J \qquad (6.15)$$

and this transformation leaves the mathemacil structure of the theory invariant. This transformation forms a continous symmetry group and this group properties are used. In logarithmic problems the analytical form of the new quantities is not altered by the transformation if the effective coupling defined by equation (6.11) is introduced thus e.g. for the function $d(\omega)$

$$d\left(\frac{\omega}{D}, J_{eff}\left(\frac{\omega}{D}\right)\right) = z_1\, d\left(\frac{\omega}{D}, J\right) \qquad (6.16)$$

As it is shown by Sólyom, this equation with energy independent Z holds even if the imaginary parts are included. For a continous group the infinitesimal transformation can be cast into the form of a Lie

equation, which is given here for the effective coupling (frequently called invariant coupling) itself:

$$\frac{\partial}{\partial \ln \frac{\omega}{\mathfrak{D}}} \ln \mathcal{J}_{eff}\left(\frac{\omega}{\mathfrak{D}}; \mathcal{J}\right) = \frac{\partial}{\partial \xi}\left[\ln \mathcal{J}_{eff}\left(\xi; \mathcal{J}_{eff}\left(\frac{\omega}{\mathfrak{D}}, \mathcal{J}\right)\right)\right]_{\xi=1} . \quad (6.17)$$

The expression on the right hand side of this equation is the infinitesimal generator of the group, where the effective coupling constant occurs in the argument. The actual calculation proceeds as (i) to calculate the generator for those cut-off values where $\mathfrak{D} \sim \omega$ (ii) to solve this equation. The main difficulty is that the infinitesimal generator can be determined only in framework of perturbation theory, thus $|\mathcal{J}_{eff}(\frac{\omega}{\mathfrak{D}}, \mathcal{J})| \ll 1$ is assumed. In the second order scaling the diagrams in figures 1o. and 27. are considered (see e.g. Fowler and Zawadowski 1971) and the scaling given by equation (6.14) is recovered.

It is worth mentioning that recently Sakurai and Yoshimori (1973) combined the most advanced variational calculation for the ground state with the dynamical renormalization group discussed before and the following ground state energy was derived

$$E_B = -\mathfrak{D}\sqrt{\mathcal{J}\rho_0/N}\, \exp\{N/2\mathcal{J}\rho_0\} . \quad (6.18)$$

The ground state energy is associated with the Kondo temperature, as it scales the temperature dependence.

The result obtained is in accordance with the expection discussed at the beginning of this section, because it is much smaller than the Abrikosov's expression $kT_K \sim D\exp\{N/2\gamma_0\}$ derived in leading logarithmic approximation. For further discussion see section 6.7.

Several consequencies of finite γ_{eff} at $\omega = T = 0$ have been discussed by Abrikosov and Migdal (1970).

In general the most striking question is whether the effective coupling tends to infinity or remains finite as ω and T tends to zero, or in other words, whether there are singular points on the scaling plane or not, depending on that the infinitesimal generator has no zeros or it has. This question can not be settled in the present schema, because in the case of strong coupling these methods break down as it has been discussed before. The arguments at the end of section 6.4 and Wilson's theory to be discussed in the next section prefer no singularity.

The dispersion theories with electron-hole pairs in the intermediate state see Maleev (1969 and 1971), Hübel (1971) seem to be even more complicated and it is hard to get reliable results.

6.5 Wilson's theory

Wilson (1973) realizing that renormalization group methods discussed in the previous section are not capable to solve the question whether the effective coupling remains finite at T=0 and ω =0 or not, has turned to a new formulation of the problem which allows to combine the renormalization group method with numerical computer calculations. It is obvious that such method should not rely on diagram representation. Wilson's aim was to establish a wawe function calculation for the ground state and its low lying excitations and to determine the eigenvalues by some numerical iteration procedure.

First of all he modified the Kondo model to fit his purposes. It was done in three steps:

(i) introducing a discretisation in the wave number of the conduction electron as $(k-k_F) \sim \pm \Lambda^{-n}$ where Λ is an arbitrary number in order of two, and n is the new quantum number. By this step the conduction electron density of states is distorded which is compensated by making the coupling n-dependent in such way that the contribution of the low lying energy states (in the neighbourhood of the Fermi energy) to the free energy is not altered. The Hamiltonian considered is

$$H = \sum_{n=0,\sigma}^{\infty} \Lambda^{-n} \left(a^{+}_{n\sigma} a_{n\sigma} - b^{+}_{n\sigma} b_{n\sigma}\right) - \mathcal{J}\left(A^{+} \vec{\sigma} A\right) \vec{S} \qquad (6.19)$$

where

$$A_\sigma = \sum_{n=0}^{\infty} \Lambda^{-n/2} (a_{n\sigma} + b_{n\sigma}) \qquad (6.20)$$

and $a_{n\sigma}$ and $b_{n\sigma}$ are the electron and hole annihilation operators, and $\vec{S}$ describes S=1/2.

(ii) a new set of basis functions is constructed by an iteration procedure in order to achieve a hopping Hamiltonian

$$H = \sum_{n=0,\sigma}^{\infty} \Lambda^{-n/2} \varepsilon_n (f_{n\sigma}^{+} f_{n+1\sigma} + f_{n+1\sigma}^{+} f_{n\sigma}) - \mathcal{J}(f_{0}^{+}\sigma f_0) \qquad (6.21)$$

where $f_{n\sigma}^{+}$ is the creation operator on site n [and $A_\sigma \sim f_{0\sigma}$]. This Hamiltonian has the form of a linear chain with sites labelled by n , the first term describes the hopping between different sites, furthermore, the second term shows that the impurity spin is coupled with those electrons sitting on site "0".

(iii) in a good approximation $\varepsilon_n = 1$.

The main idea is that the hopping element far from the spin do not modify the spectrum in an essential way. Keeping only a few neighbours of the spin to retain only about 2oo-5oo states one could diagonalize the problem by computer. In the following step one more neighbour is included and about 1oo-3oo states is dropped from those which have already been computed to keep the same number of states as in the previous step.

Diagonalizing again and again by performing 5o to 8o iterations a reliable energy spectrum is obtained. Without going into details of the computation and accuracy, we confine ourselves only to the conclusion. The spectrum obtained was compared with that which corresponds to a similar Hamiltonian but without the spin $\vec{S}$ and site n=0. It was turned out that these two spectra coincide with a great accury for the lowest states.

This result can be interpreted as if the impurity and the electron on site n=0 were glued together with infinite coupling $\mathcal{J}_{eff}^{(\omega=0)=\infty}$ to form a singlet. The other electrons behave like a free gas because their energy is not strong enough to break this singlet formed on site n=0.

In order to describe the excited states Wilson introduced a phenomenological extra Hamiltonian acting on the electron gas but not on the singlet. The parameters of this pseudo Hamiltonian have been fitted to reproduce the spectrum calculated numerically and, afterwards, this spectrum has been extrapolated to excitations with higher energies. In this way the heat capicity $C_{imp}^{(T=0)}$ and the magnetic susceptibility have been evaluated as well. The result can be summarized as

$$\chi_{imp}(T=0) \simeq \frac{1}{D} \frac{1}{\sqrt{2\mathcal{J}\rho_0}} \exp\left\{\frac{1}{2\mathcal{J}\rho_0} + 1.58(2\mathcal{J}\rho_0)\right\} \quad (6.22)$$

and

$$\lim_{T\to 0}\left\{\frac{C_{imp}(T)}{T\chi_{imp}(T)}\right\} = \frac{2\pi^2}{3}(1\pm 0.3)k_B \quad (6.23)$$

where k_B is the Boltzmann's constant. This J-dependence is a result of numerical fit of data obtained with different coupling strenth J.

Wilson's theory strongly indicates that in the scaling theories $\mathcal{J}_{eff}$ should increase beyond any limit and that is widely accepted as the final answer.

The question of the Kondo temperature is left to section 6.7. Furthermore it is still not clear what is the meaning of the "Toulouse limit" is this theory.

6.6 Functional integral method.

The functional integral method was hoped to fill the gap between the theories based on the s-d and Anderson models. The starting point is a mathematical identely

$$e^{a^2} = \int_{-\infty}^{\infty} dx \exp\left\{-\pi x^2 - 2\pi^{1/2} a x\right\} \quad (6.24)$$

which holds even if "á" is an operator. This formula gives a possibility to linearize a squared term in an

exponent, but an additional integral occurs.

This formula may be applied to the calculation of partition function

$$Z \sim \langle T_\tau \exp\left[-\int_0^\beta d\tau\, H_1(\tau)\right]\rangle \qquad (6.25)$$

where $\beta = \frac{1}{kT}$ and τ is the complex time variable, furthermore, the interaction Hamiltonian is given in interaction representation. Having the integral with respect to τ in the partition function in equation (6.24) "a" would be τ-dependent and thus the integral becomes a functional integral.

The Anderson model is very appropriate for applying this identity as the Coulomb integral term $U n_{d\uparrow} n_{d\downarrow}$ can be written in the form of squared expressions in different ways e.g.

$$U n_{d\uparrow} n_{d\downarrow} = \frac{1}{4} U (n_{d\uparrow} + n_{d\downarrow})^2 - \frac{1}{4} U (n_{d\uparrow} - n_{d\downarrow})^2 \qquad (6.26)$$

Applying the indentity discussed above for both terms a double functional integral is obtained. The idea behind this formal step is that the interaction can be replaced by the problem of free particles moving in fluctuating classical fields acting on the combinations $n_{d\uparrow} + n_{d\downarrow}$ and $n_{d\uparrow} - n_{d\downarrow}$. Thus, two fields act on the charge and magnetization fluctuations respectively.

There are, however, statistical weights for the different field fluctuations to control the dynamical behaviour. In actual cases it is very hard to perform the functional integrals. The method in the context of the Anderson model was used by Evenson, Wang and Schrieffer (197o) and Hamann (197o) . The first succes has been that the H.F. solution can be easily recovered restricting the possible paths to the time independent one. It turned out, however, that it is very difficult to reproduce even a single logarithmic term by this method (see discussion and further references at Amit and Keiter 1973) . On the other hand, in the strongly magnetic regime of the Anderson model, Hamann (197o) succeeded to relate this method to the Anderson-Yuval-Hamann scaling (see section 6.3) by evaluating the functional integral in a particular regime of the paths which correspond to the spin-flip scattering. Furthermore, Hertz (1971) applied this method in the non-magnetic regime of the Anderson model to achieve scaling by eliminating the contribution of the highest frequency random field from the functional integral, for further discussion see section 3.4 . Inspite of this success, the results remained far from the expectations. We may, finally, mention that Yoshimori and Sakurai (197o) applied this method to the s-d model and the most divergent terms were reproduced.

6.7 Comporison and problems to be solved

Concerning the Anderson model the theoretical part of the problem has not been developed in a satisfactory manner. The study of the s-d model reached however, a stage where the phenomena have already been well understood and the theoretical description has improved in a significant way.

By taking the excitation of electron-hole pairs into considerations it has been demonstrated at least that the high temperature logarithmic behaviour is changing to a power dependence at low temperatures. The weak coupling problem becomes stronger by decreasing the temperature and according to the new developments in the theory the effective coupling tends to infinity at $T = \omega = 0$. The characteristic temperature where the stronger effective coupling enters can be called the Kondo temperature. Starting from high temperature the new T_k can be defined as the temperature where according to the dynamical scaling laws (equation 6.14) the medium strong coupling occurs e.g. where $0.2 < \gamma_{eff} < 0.5$. This can be easily determined by using equation (6.14) and calculating the corresponding energy value $\omega = k T_k^{new}$, thus one finds

$$k T_k^{new} \approx D \sqrt{2\gamma\rho_0 / N}\, \exp\left\{ \frac{N}{2\gamma\rho_0} \right\} \qquad (6.24)$$

This expression seems to be in agreement with the expression of the binding energy E_B derived by Sakurai and Yoshimori (1973) given by equation (6.18) and furthermore, with the susceptibility fitting Wilson's numerical results (see equation 6.22) as the binding energy and the inverse susceptibility are expected to be proportional to the characteristic scaling temperature. It disagrees, however, with that obtained from the thermodynamical scaling laws by Anderson and Armytage (Anderson 1973) where the factor $(2\pi\rho_0/N)^{1/2}$ is replaced by $(2\pi\rho_0/N)^{3/2}$. This is probably due to the approximate treatment of the cut-off procedure which may play a crucial role in the case of stronger coupling. Summarizing this result, we may conclude, that in the weak coupling limit the expression given above is correct and it predicts a much smaller Kondo temperature than that occuring in the one particle intermediate state approach see equation 4.26.

For low temperature the dynamics is not yet worked out. On the basis of Wilson's new result that at T=0 the impurity is glued to the electron at the site n=0 in hopping model, it is expected, that at T=0 all of the physical properties are analytical and simple power expansions are adaquate. Hence, the electrical resistivity should be given by a simple Sommerfeld expansion, thus it should show a T^2-dependence (see for further discussion Anderson 1973 and Fowler 1972). This behaviour at low temperature may be called spin fluctuation

in the sence that the thermal fluctuations in the Kondo state result in the appearance of a small magnetic moment. The T^2-dependence ~~in the~~ LSF theory based on the existence of localized paramagnons (see discussion in section 3.3). It must be, however, emphasized that the detailed dynamics producing the resonance with Lorentzian behaviour at small energies are rather different in the two theories. Therefore, although there are formal similarities and in both cases there are thermal fluctuations in ~~A~~ non-magnetic states the ground states in the two models are so different that the parameters of the resonances can be connected only in a formal way but without physical ground.

Considering the future, the main task is to find a theoretical description and more detailed justification for the Lorantzian behaviour ~~of~~ at the top of the Abrikosov-Suhl resonance.

7.CONCLUSIONS

In this review we confined ourselves to those aspects of the dilute alloy problem which were important for the understanding of the resonance formation,and therefore many questions,rather interesting on their own right,were not discussed as they are not related directly to this problem.

In particular the behaviour of the impurities in a superconducting metal was not mentioned,mainly because it appears,that the formation of the resonances is the result of more complicated processes than in normal metals,as the host density of states exhibits a charactersitic structure the energy gap near to the Fermi energy,and a high density of states near to the treshold of the gap.As the Kondo temperature can be larger or smaller that the superconducting transition temperature T_c ,widely diverging phenomena are expected,and found,depending on the ratio of the two characteristic temperatures.The experimental status is reviewed by Rizzuto (1974) the theoretical developments by Müller-Hartmann (1974).An other field,which attracted wide interest, but was not discussed here,is the metal - metal oxide - metal junctions with paramagnetic impurities in or near to the barrier.The physical phenomena are twofold:the impurity assisted tunneling suggested by Appelbaum (1967) and the change of the electron density of states near to or in the impurity layer, the latter can be discussed in a similar way than for a single impurity (for references see Mezei and Zawadowski 1971b).The sample preparation however is rather difficult,and therefore the real cause of the anomalies found in the I-V characteristics is still unclear.The relaxation pheomena in dilute alloys

were also not discussed, in spite of it was believed for a long time that these pheomena can give rather valuable information on the dinamical behaviour of the impurities. It appears howewer that the s-d interaction has not a dominant role here, because the spin of the impurity and the conduction elecrons enters into the dynamics as a whole, if the gyromagnetic factors are the same, this effect is known as "bottleneck". The experiments howewer give information on the spin-lattice relaxation (see for example Monod and Schultz 1968). The same can be said for the dynamical susceptibility (see Götze and Schlottmann 1973 and references cited therein), which is connected to the neutron scattering experiments, which should show a maximum at energy transfers near kT_K (Gurgieshvili et al 1969). The effect of magnetic field on the Kondo scattering was not reviewed too, and only the giant negative magnetoresistance was mentioned. It is howewer clear, that an external magnetic field makes the spin-flip scattering inelastic, and therefore the effect of external field should show up in side bands near to the energy μH, the internal magnetic field due to impurity-impurity interactions leads to similar effects.

The other aspect which was left out is the influence of anysotropy, crystalline field splitting, spin-ordit interaction, and the influence of the orbital degeneracy on the Kondo scattering. It appears that while these effects may lead to a slight modification of the scattering problem, they do not play such a crucial role here than for impurities with an unfilled 4f shell. Furthermore it appears, that the orbital degeneracy is not fundamental and the non-degenerate model works well if one replaces U by $U + 4J$, although the

theoretical background for this is not clear.

Phenomenological models which attempt to account for the Kondo behaviour should also be mentioned, in particular Souletie's (197o) suggestion that the temperature dependences of the transport properties can be described by temperature dependent phase shifts $\delta_\sigma(T)$, which correspond to the non-magnetic HF spolution at T=0 and to a magnetic HF solution at $T \gg T_K$. It is clear that a phase shift analysis works at zero temperature, and also gives some information on the scattering at very high temperatures when spin-flip is properly included. A description in terms of phase shifts is howewer questionable at low temperatures, if it is used to account for temperature dependent effects. Assuming that the scattering amplitude is an analytic function of T around 0^oK, one can make a power expansion of equation (4.34). Keeping only the one particle scattering amplitudes, the temperature dependence has a leading T^2 term and futhermore if $|\tau|^2$ can be neglected in (4.34) then $|t|$ can be expressed in terms of the phase shift $\delta(T)$, what means that τ does not contain linear terms. This howewer has no firm theoretical background.

In spite of many theoretical details of the Kondo problem are still unsolved we believe that the formation and the nature of the narrow and broad resonances is basically understood. Among questions which still await a solution, the experimental evidence of the spatial distribution of the conduction elecron - impurity spin correlation function discussed in section 4.10 should be mentioned. Theoretically the most important question remained is to work out tha dynamical scaling laws in order to describe the to of the Abrikosov-Suhl resonance and to justify it's T^2 or ω^2 dependence, such calculation

would also give the electrical resistivity for example.

Finally one should stress that although the dilute alloy problem can be regarded as perhaps the most beautiful example how localization and delocalization occurs, and how single particle and many particle resonances combine together, the main concepts are not unique and can be applied for other branches of physics. In particular chemisorption and molecular reactions were discussed using rather similar models and theoretical methods. As far as the progress towards the understanding of the broader aspects of 3d magnetism is concerned definite steps have been taken for the description of more concentrated disordered alloys (which are often called spin glasses, see for example Coles 1973) or ordered intermetallic compounds (Caplin and Dunlop 1973). In both cases the Kondo behaviour is combined with interaction effects, thus giving rise to a broader variety of phenomena than in the case of single impurities. Investigations of such systems may also bridge the gap between the two well studied aspects of metallic magnetism: the Kondo effect and the highly correlated electron gas.

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Fig.9.General form of the conduction electron - impurity spin vertex function with one electron or hole excitation in the intermediate state.The solid line represents electrons the dotted line the pseudofermions and the circle is the vertex.

Fig.10 a.The first order corrections to the vertex.

10 b.The second order corrections to the vertex.(the directions of the lines are not indicated).

Fig.11.Energy dependence of the phase shifts for up and down spin electrons in Anderson's construction of the ground state.The solid line is the HF solution and the dotted line represents the modification due to the Kondo effect.

Fig.12.The two possible processes (i) and (ii) of the scattering of a conduction electron on a singly occupied impurity level.The shaded region is the Fermi sea,the d-levels are labeled by 'd' and the transitions are shown by double arrows. The black circles are the electrons taking part in the scattering.

Fig.13.Amplitude of the charge perturbation $a(r)$ as a function of r/ξ_Δ .The parameter $\lambda = \frac{\omega_0}{\Delta} = ctg\,\delta_\ell(0)$ characterizes the position of the resonance (Mezei and Gruner 1972).

Fig.14.Radial dependence of the charge perturbation derived from the s-d model (Bloomfield et al 1969).

Fig.15.A schematic plot of the scattering amplitude (solid line) which shows a structure with a width $\delta\omega$ at the Fermi level.At distances $r \ll \xi_{\delta\omega}$ the charge perturbation amplitude $a(r)$ is related to a scattering amplitude $\bar{t}(\omega)$ smeared out on a scale $\delta\omega$ (dotted Line).

Fig.16.Virtual bound states of 3d impurities in gold inferred from the optical experiments.

CAPTIONS

Fig.1.Potential around the impurity with a deep hole in the center and with a potential barrier $\frac{l(l+1)}{r^2}$ .The position of the resonance is also represented.

Fig.2.Extra density of states associated with an iron impurity in copper.(Anderson and McMillan 1967).

Fig.3.Self-consistency plot of $\langle n_- \rangle$ versus $\langle n_+ \rangle$
(i) typical magnetic case with $U/\Delta = 5$, $\varepsilon_d/U = -1/2$.
(ii) A non-magnetic case, $U/\Delta = 1$, $\varepsilon_d/U = -1/2$.

3.b. Magnetic and non-magnetic regimes as a function of $(U/\pi\Delta)^{-1}$ and $-\varepsilon_d/U$.

Fig.4.The density of d-states for the two spin directions σ and $-\sigma$ in the HF approximation.The total density of states is represented by the dotted line.The occupied regions are shaded in different ways.

Fig.5.The simplest diagrams which contribute to the electron--electron (a) and electron-hole (b) correlations.The solid lines represent electrons or holes,the Coulomb interaction is represented by dotted lines.

Fig.6. HF density of states as a function of energy for a magnetic case.The density of states at the Fermi level as predicted by the charge neutrality (small circles) are shown for Fe,Mn and Cr impurities.

Fig.7.The two possible modifications of the HF density of states for T=0 which satisfies the charge neutrality condition.

Fig.8.Two time ordered diagrams corresponding to the conduction electron scattering amplitude in second order of perturbation theory.The solid lines represent electrons or holes the dotted lines with a cross at the end the exchange interaction.

Fig.9.General form of the conduction electron - impurity spin vertex function with one electron or hole excitation in the intermediate state.The solid line represents electrons the dotted line the pseudofermions and the circle is the vertex.

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10 b.The second order corrections to the vertex.(the directions of the lines are not indicated).

Fig.11.Energy dependence of the phase shifts for up and down spin electrons in Anderson's construction of the ground state.The solid line is the HF solution and the dotted line represents the modification due to the Kondo effect.

Fig.12.The two possible processes (i) and (ii) of the scattering of a conduction electron on a singly occupied impurity level.The shaded region is the Fermi sea,the d-levels are labeled by 'd' and the transitions are shown by double arrows. The black circles are the electrons taking part in the scattering.

Fig.13.Amplitude of the charge perturbation $a(r)$ as a function of r/ξ_Δ .The parameter $\lambda = \frac{\omega_0}{\Delta} = ctg\,\delta_\ell(0)$ characterizes the position of the resonance (Mezei and Gruner 1972).

Fig.14.Radial dependence of the charge perturbation derived from the s-d model (Bloomfield et al 1969).

Fig.15.A schematic plot of the scattering amplitude (solid line) which shows a structure with a width $\delta\omega$ at the Fermi level.At distances $r \ll \xi_{\delta\omega}$ the charge perturbation amplitude $a(r)$ is related to a scattering amplitude $\overline{t}(\omega)$ smeared out on a scale $\delta\omega$ (dotted Line).

Fig.16.Virtual bound states of 3d impurities in gold inferred from the optical experiments.

Fig.17.Room temperature impurity resistivities in Au and Cu based alloys.

Fig.18.Impurity resistivities at T=930°K in Al based alloys (Kedves et al 1973).

Fig.19. $\mathcal{J}$ values evaluated from the line broadening of the host NMR signal.

Fig.20.Temperature dependence of R in various alloys in a reduced temperature scale (Rizzuto et al 1973).

Fig.21.Temperature dependence of the effective moment in AuV alloys (van Dam et al 1972).

Fig.22.Impurity resistivities normalized to the $\mathcal{R}_o$ values extrapolated to T=0 for Au,Cu and Al alloys.(Grüner and Zawadowsli 1972).

Fig.23.Temperature dependence of the impurity resistivity in $Cu_xAu_{1-x}Fe$ alloys (Loram et al 1969).

Fig.24.Radial dependence of the charge perturbation around Mn and Cr impurities in aluminium.The full line is calculated with Γ =0.5eV as explained in the text (From Berthier and Minier 1973).

Fig.25.Kondo temperatures of 3d impurities in Cu and Au hosts.For references see Rizzuto (1974) and Grüner(1974)

Fig.26. Self-energy and vertex correction which are not included in the parquet approximation in thisrd order of the perturbation theory.

Fig.27. The "envelope" diagram which is beyond the scope of the X-ray absorbtion theory worked out by Nozières et al (1969).

Fig.28. Anderson-Yuval scaling curves for the anisotropic Kondo problem. The straight line corresponds to the isotropic case and the arrows indicate the scaling directions,

Fig.29. Plot of the invariant coupling as a function of energy in dynamical scaling law. Dotted line: Abrikosov's result, solid line: result obtained with infinitesimal generator calculated up to second order.

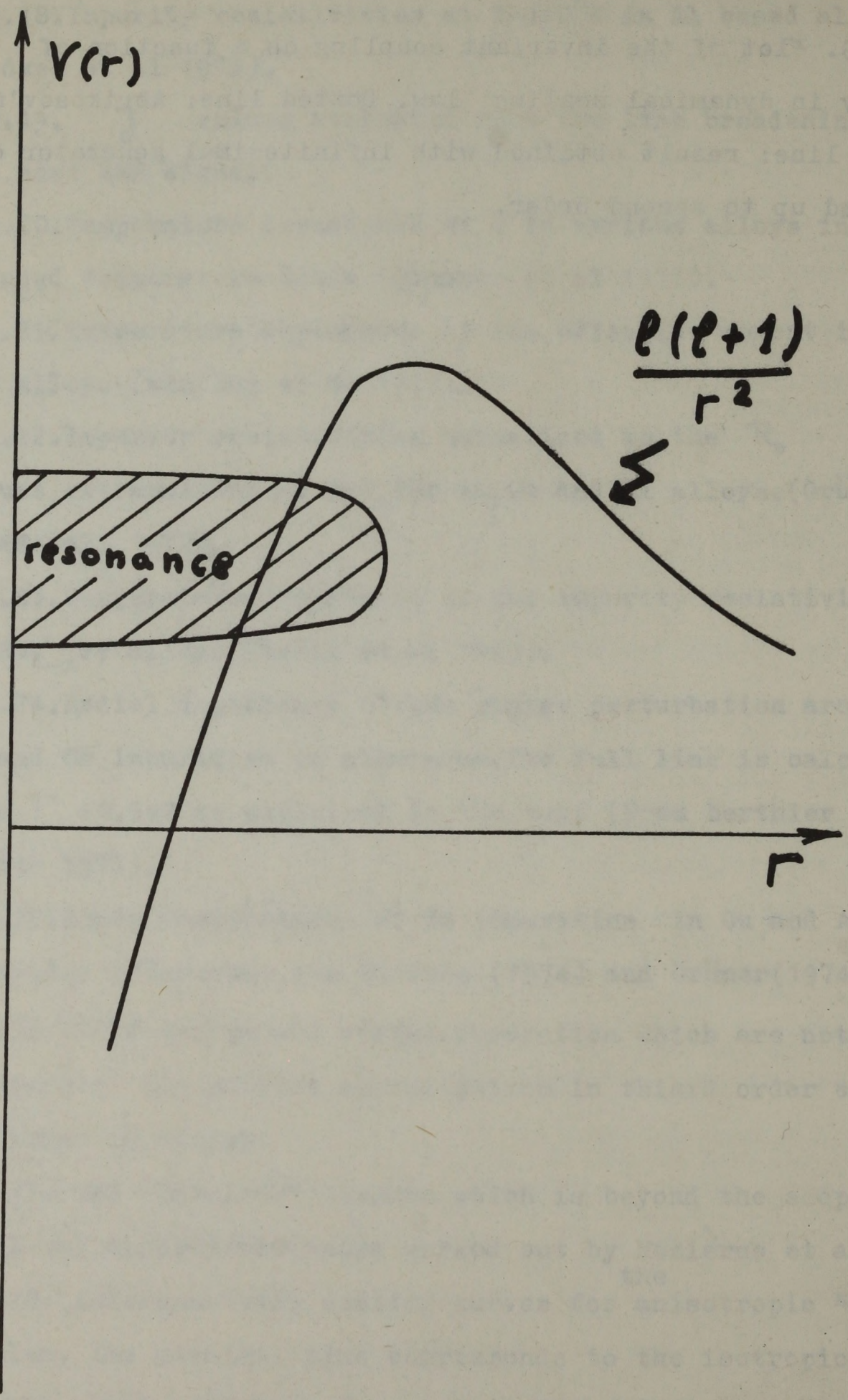


Fig. 1.

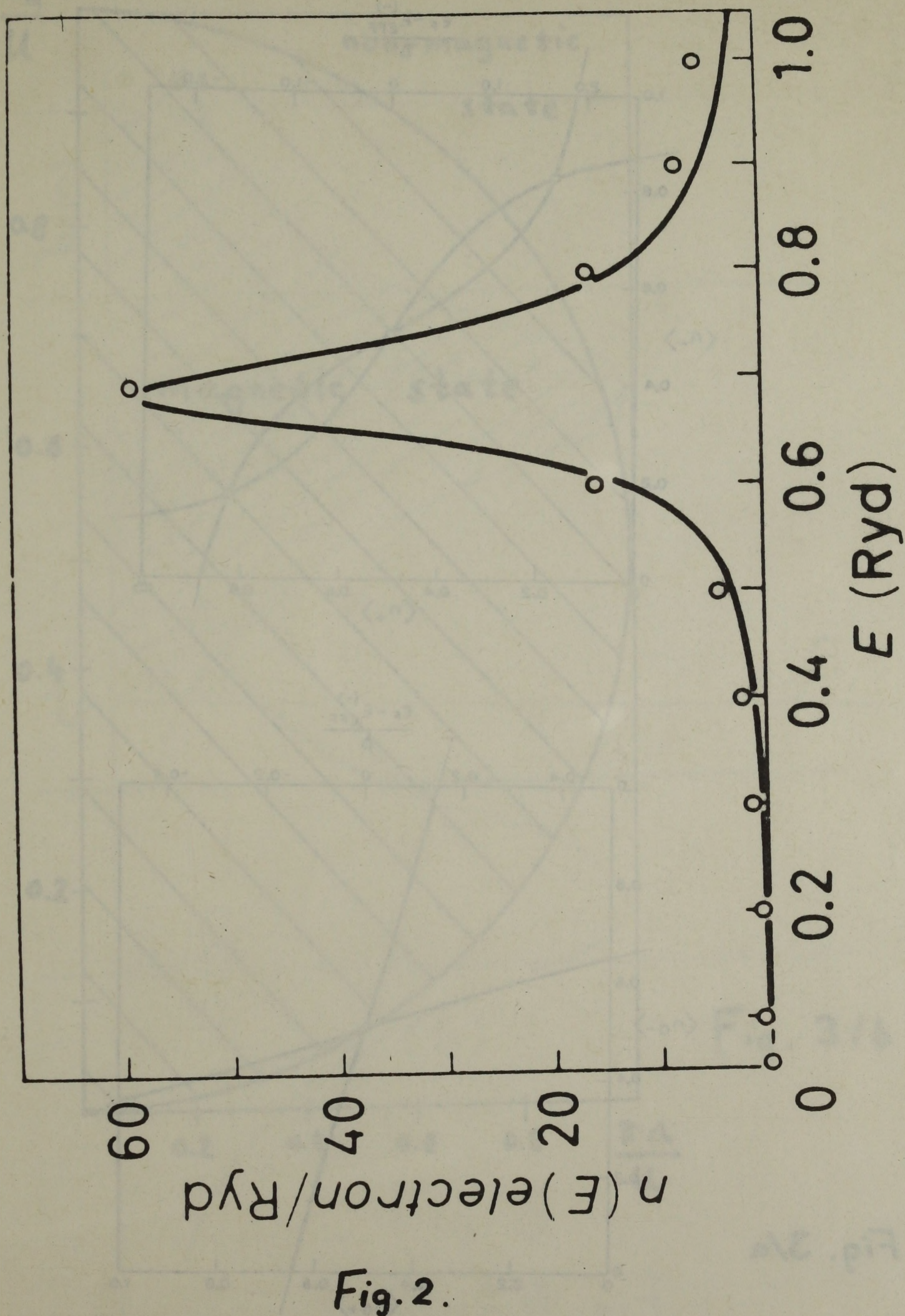
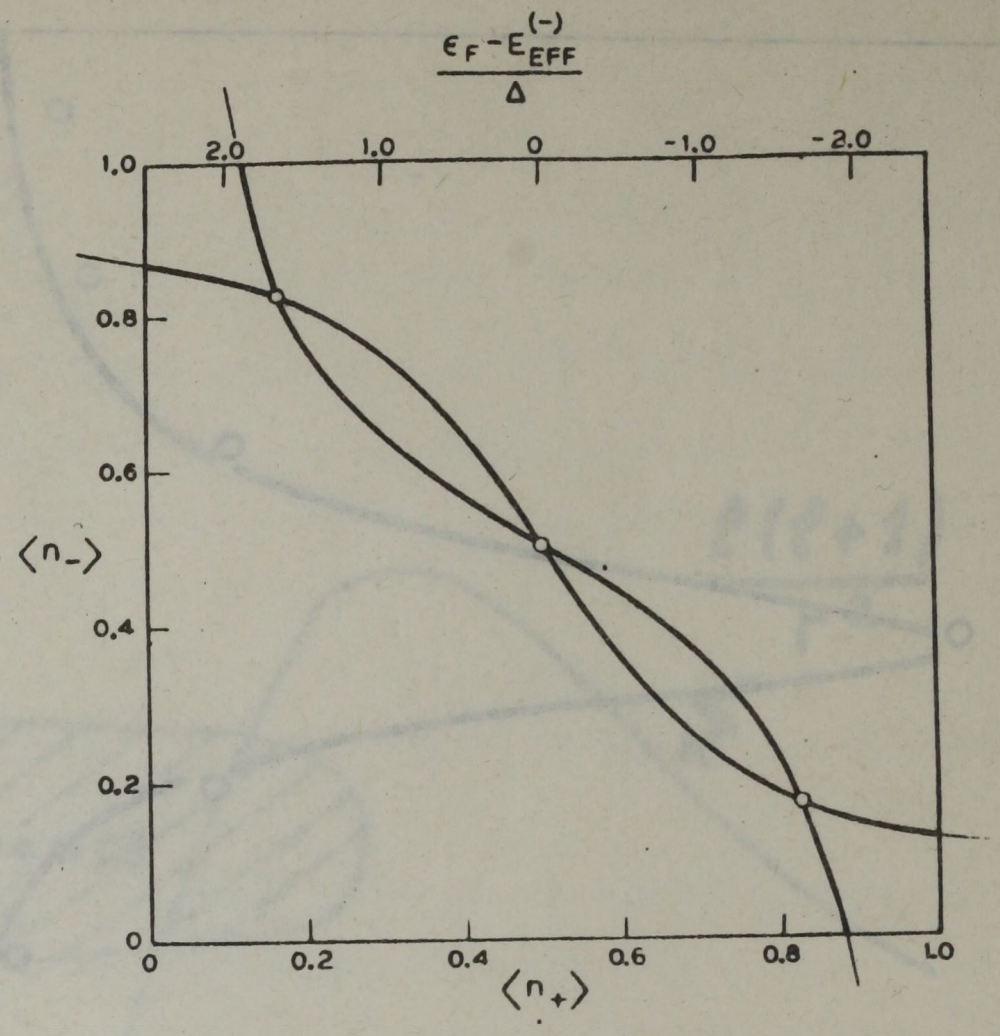


Fig. 2.


$\frac{\epsilon_F - E_{EFF}^{(-)}}{\Delta}$
2.0
1.0
0
-1.0
-2.0
1.0
0.8
0.6
0.4
0.2
0
$\langle n_- \rangle$
0
0.2
0.4
0.6
0.8
1.0
$\langle n_+ \rangle$

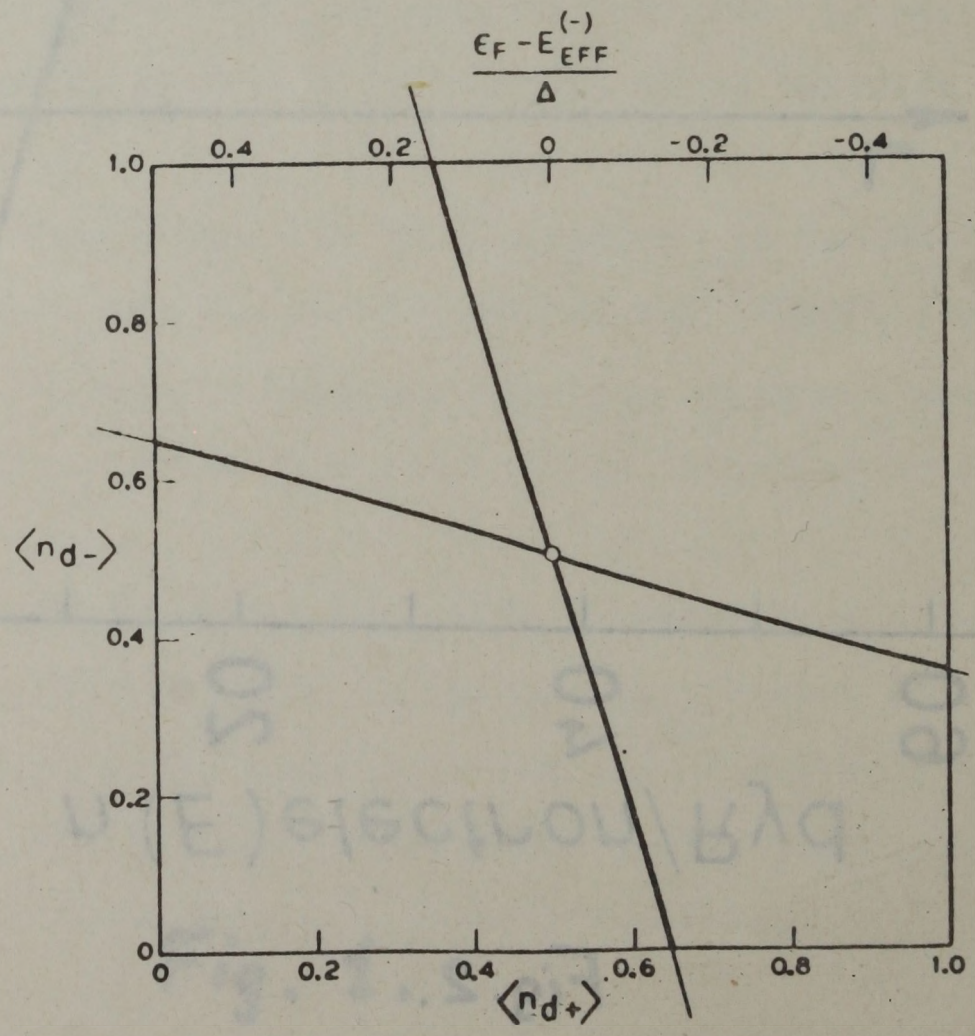

$\frac{\epsilon_F - E_{EFF}^{(-)}}{\Delta}$
0.4
0.2
0
-0.2
-0.4
1.0
0.8
0.6
0.4
0.2
0
$\langle n_{d-} \rangle$
0
0.2
0.4
0.6
0.8
1.0
$\langle n_{d+} \rangle$

Fig. 3/a

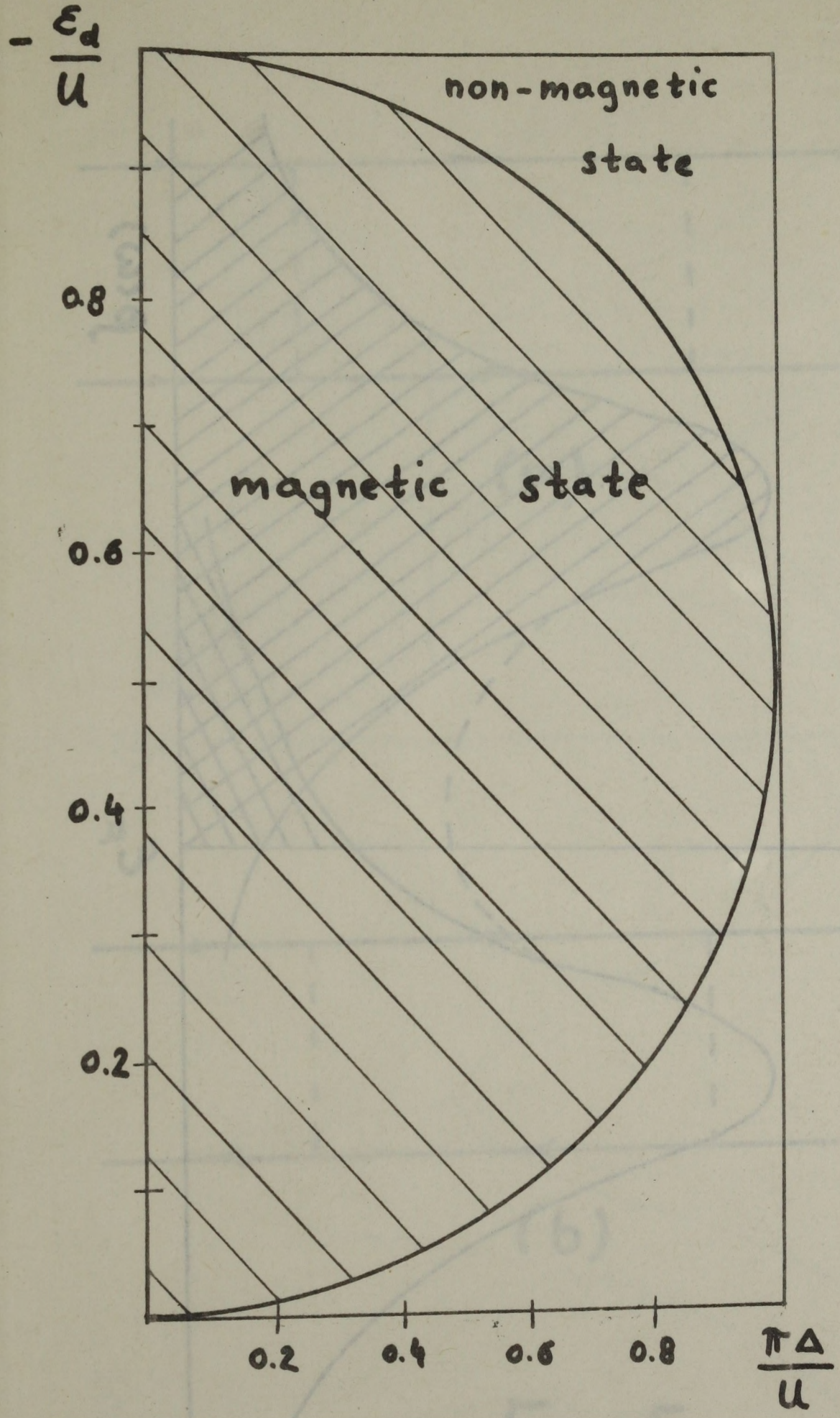

$-\frac{\varepsilon_d}{U}$
non-magnetic
state
magnetic state
0.8
0.6
0.4
0.2
0.2
0.4
0.6
0.8
$\frac{\pi\Delta}{U}$

Fig. 3/b

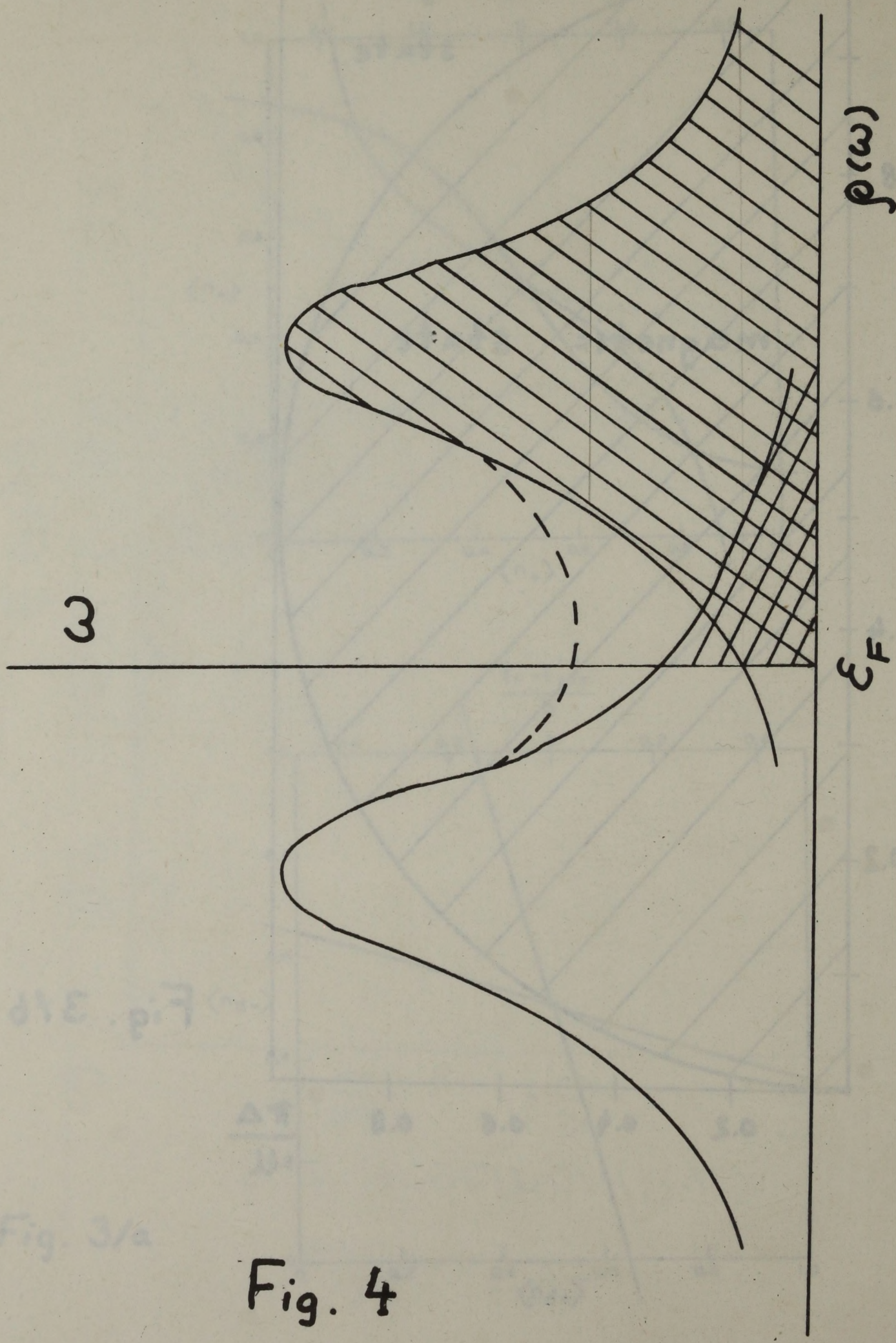
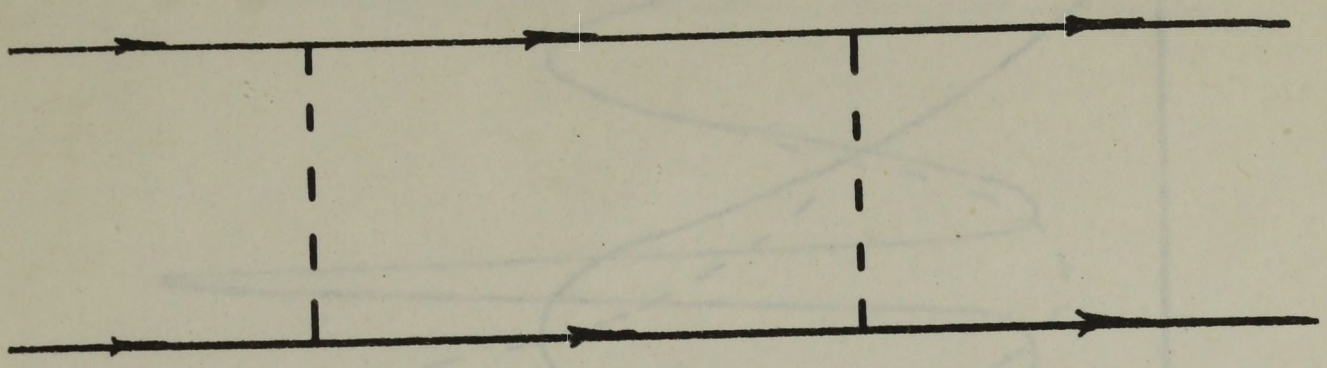
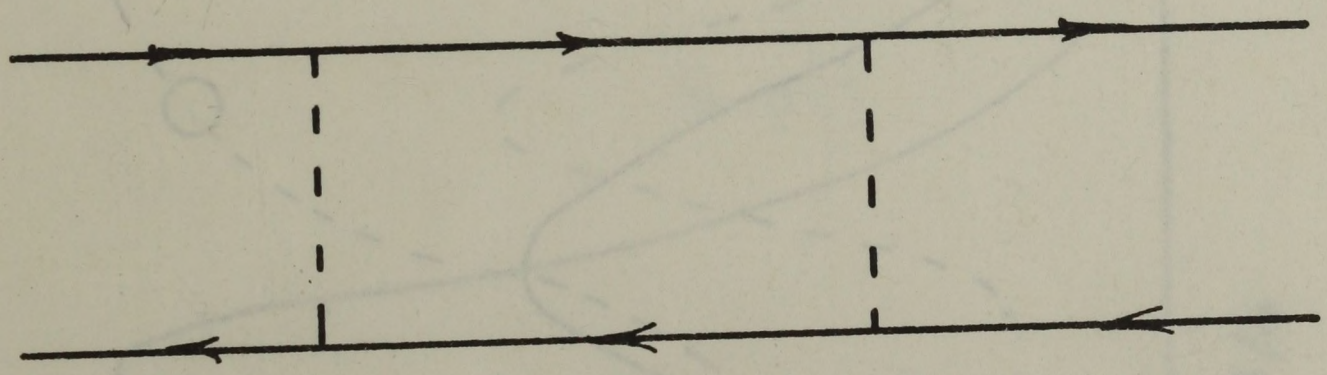


Fig. 4



(a)



(b)

Fig. 5

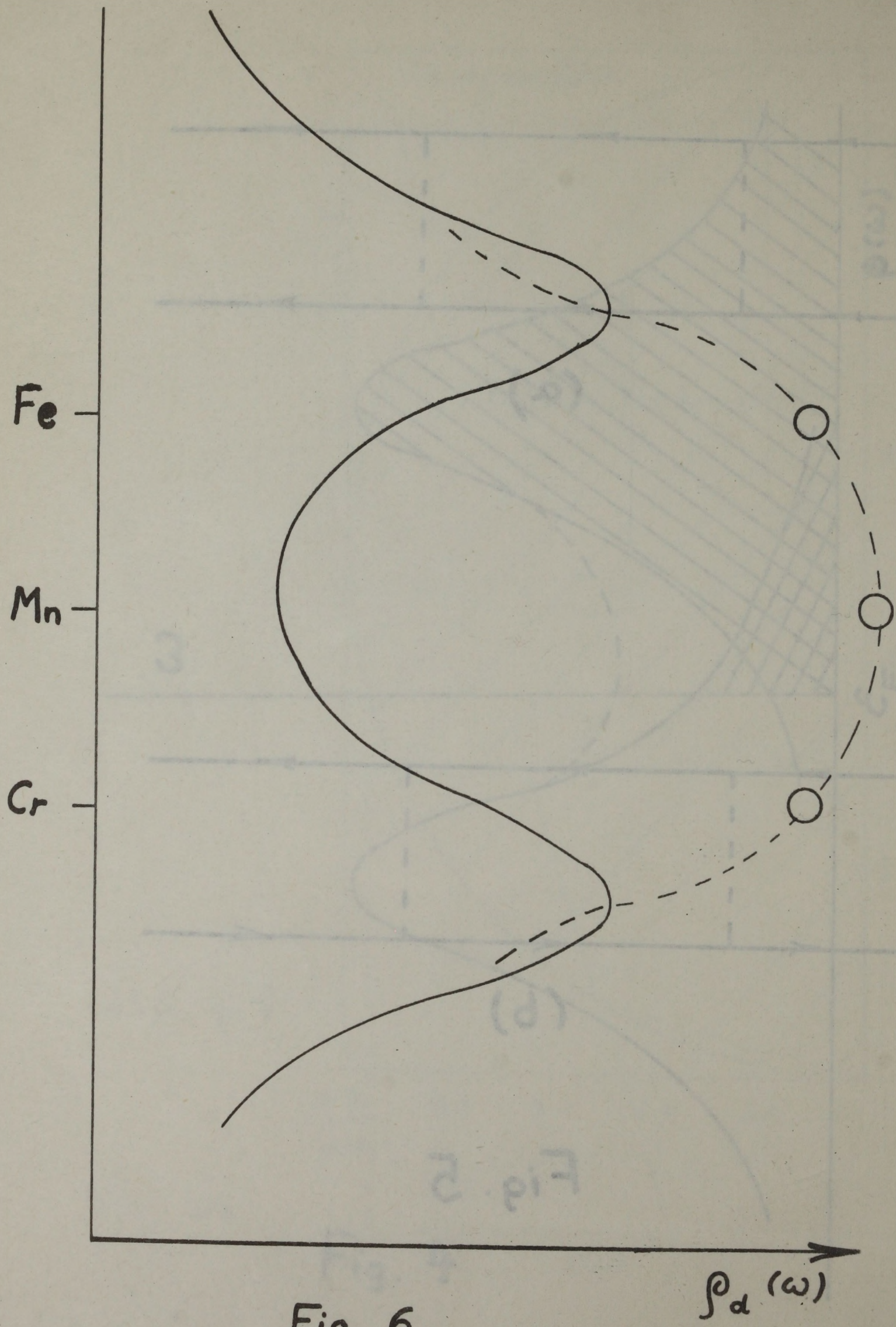


Fig. 6

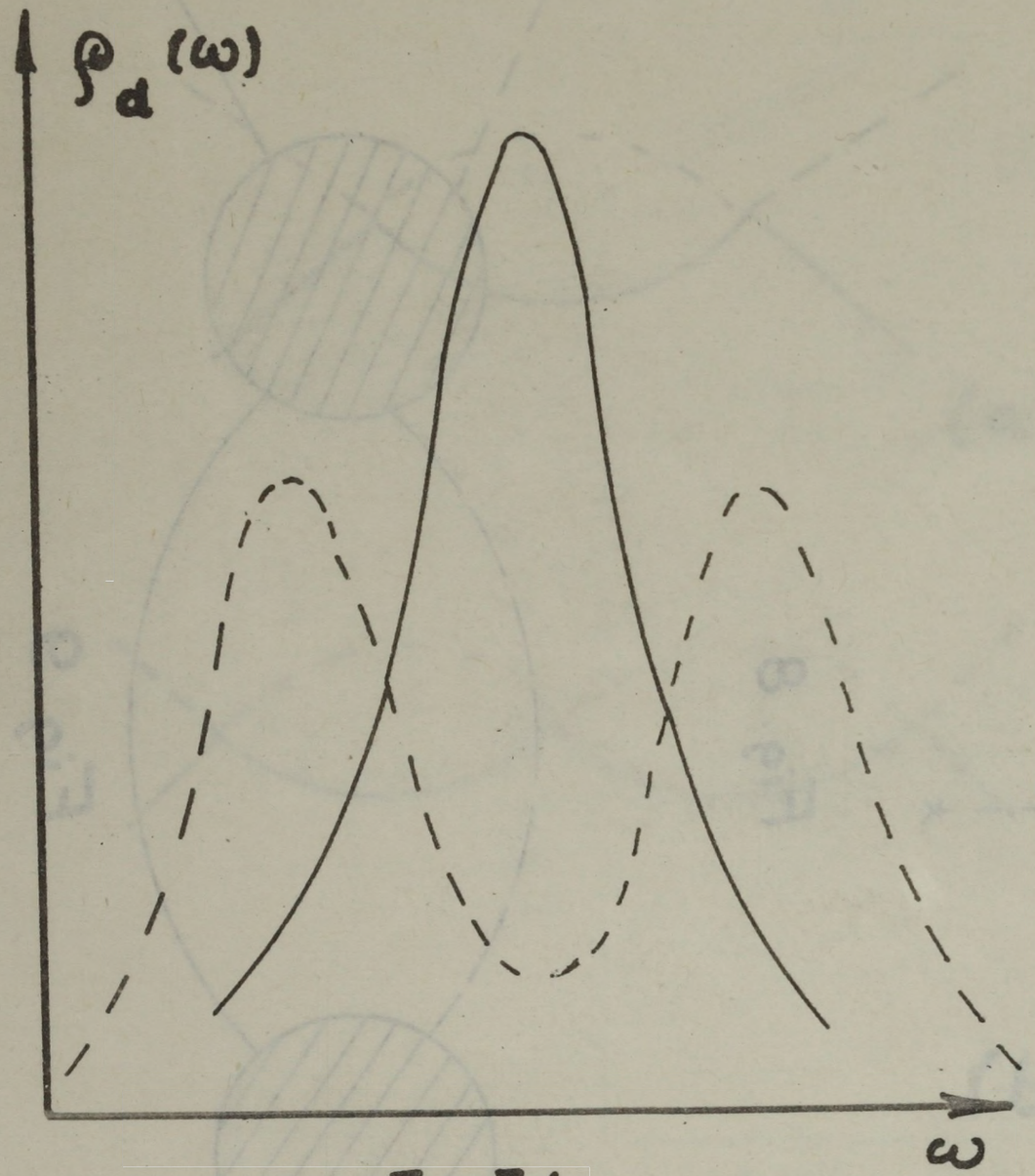


Fig. 7/a

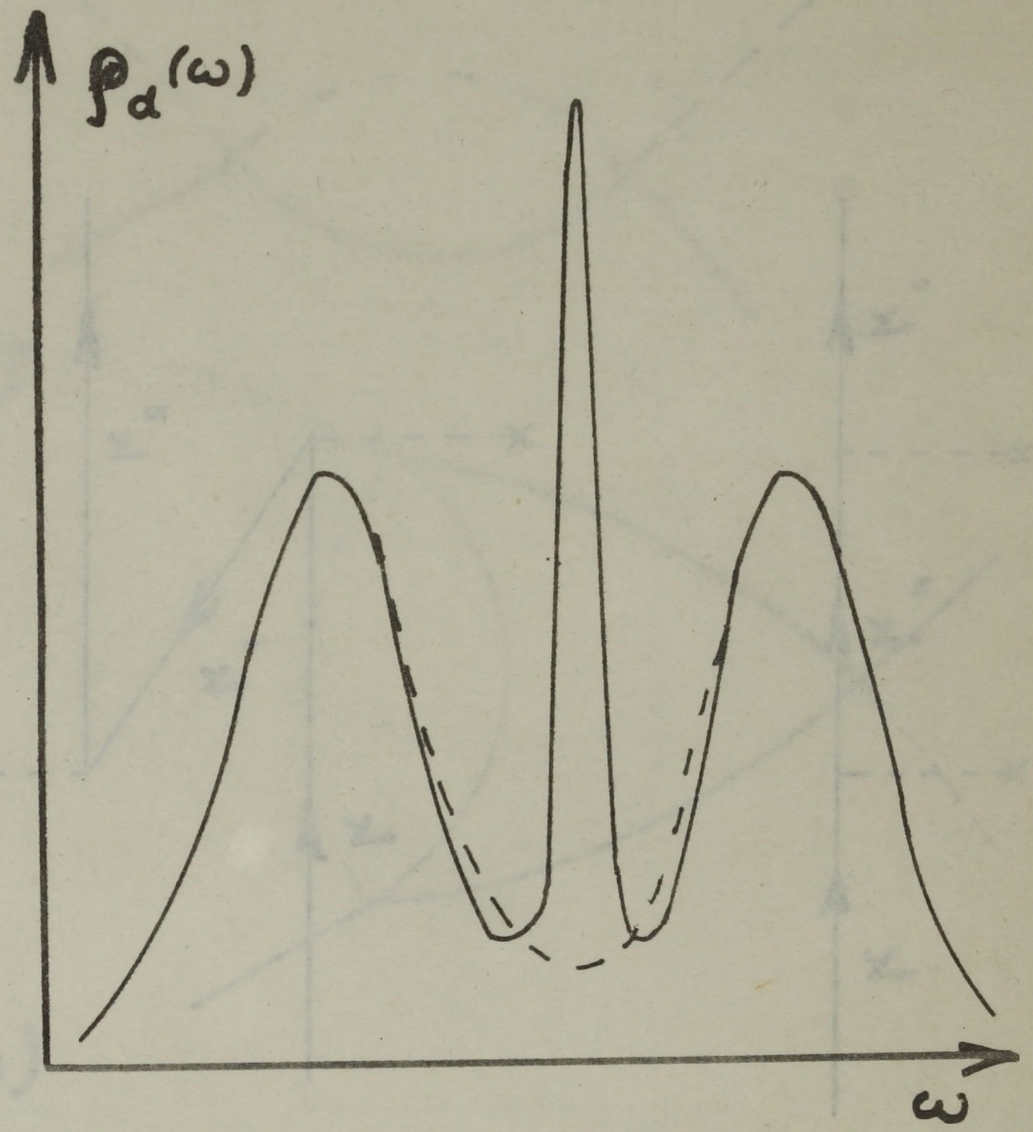


Fig. 7/b

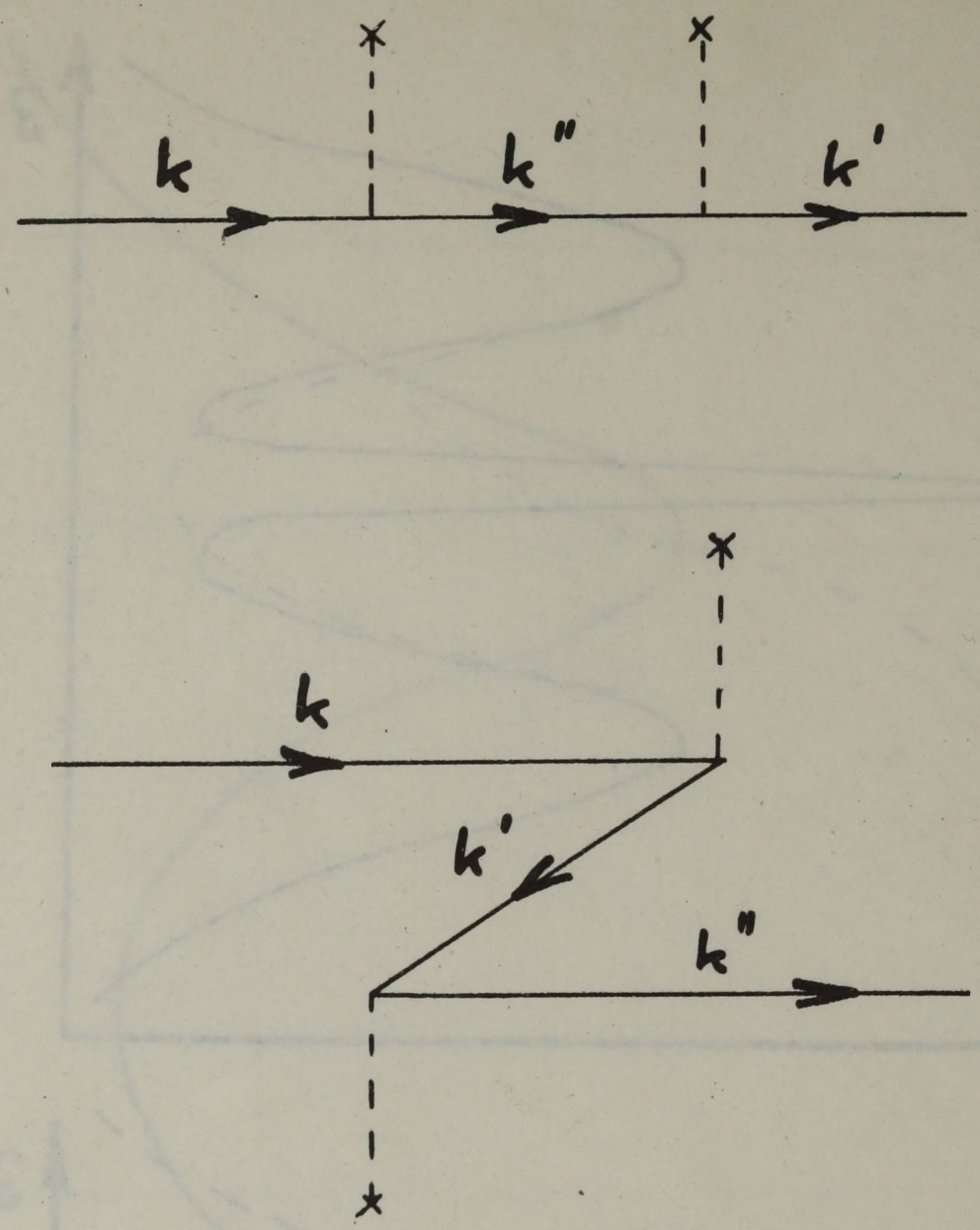


Fig. 8

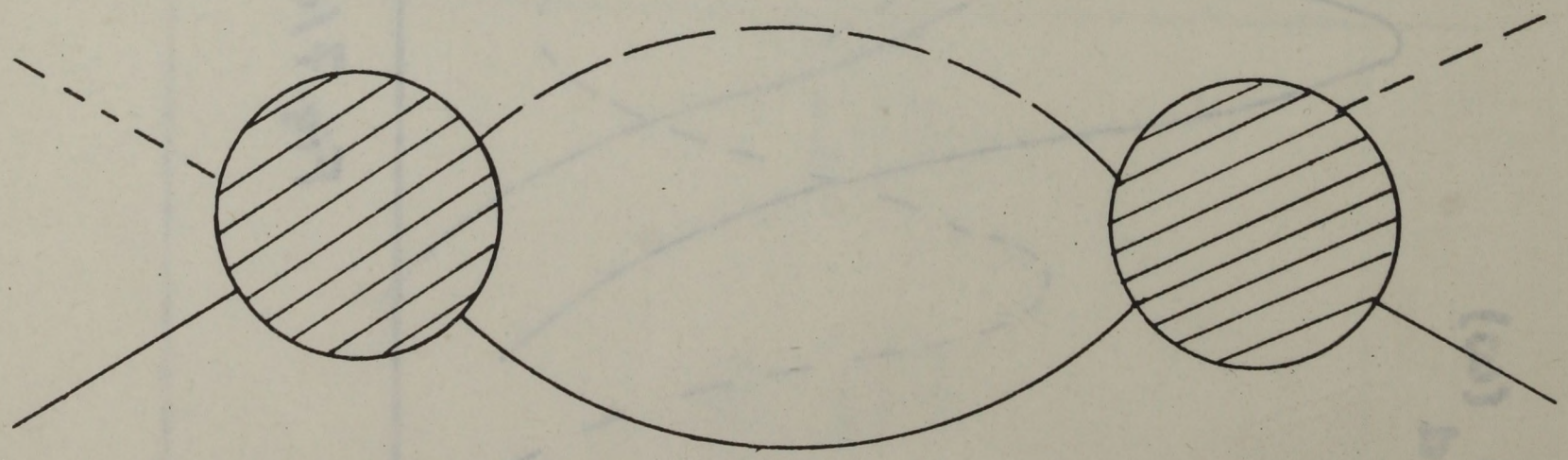
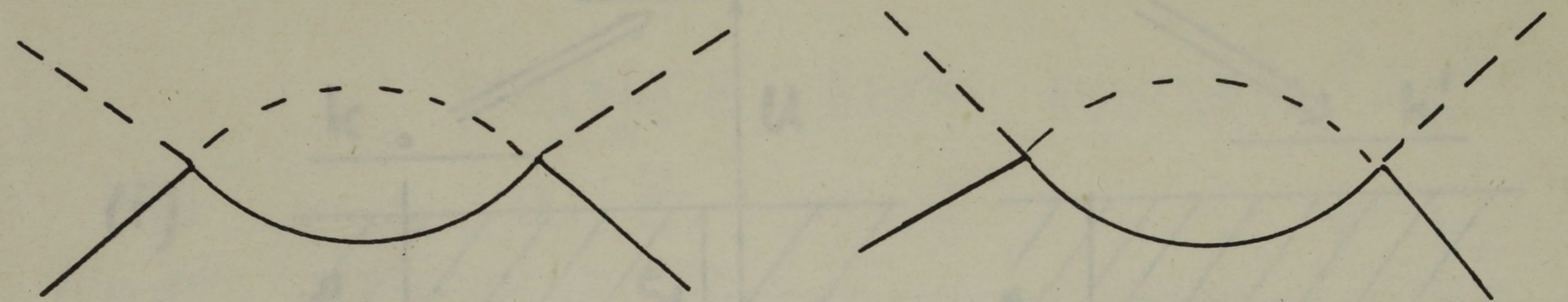
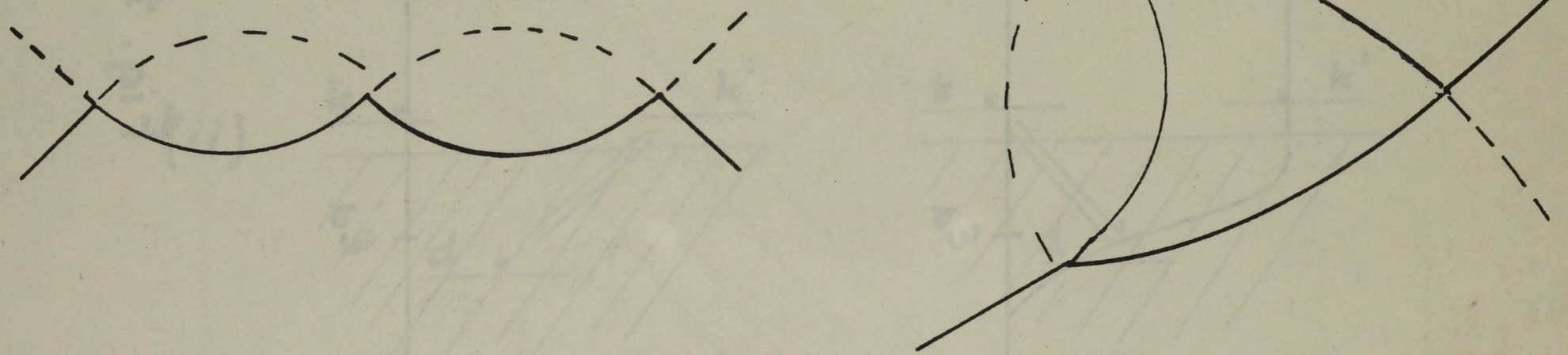


Fig. 9

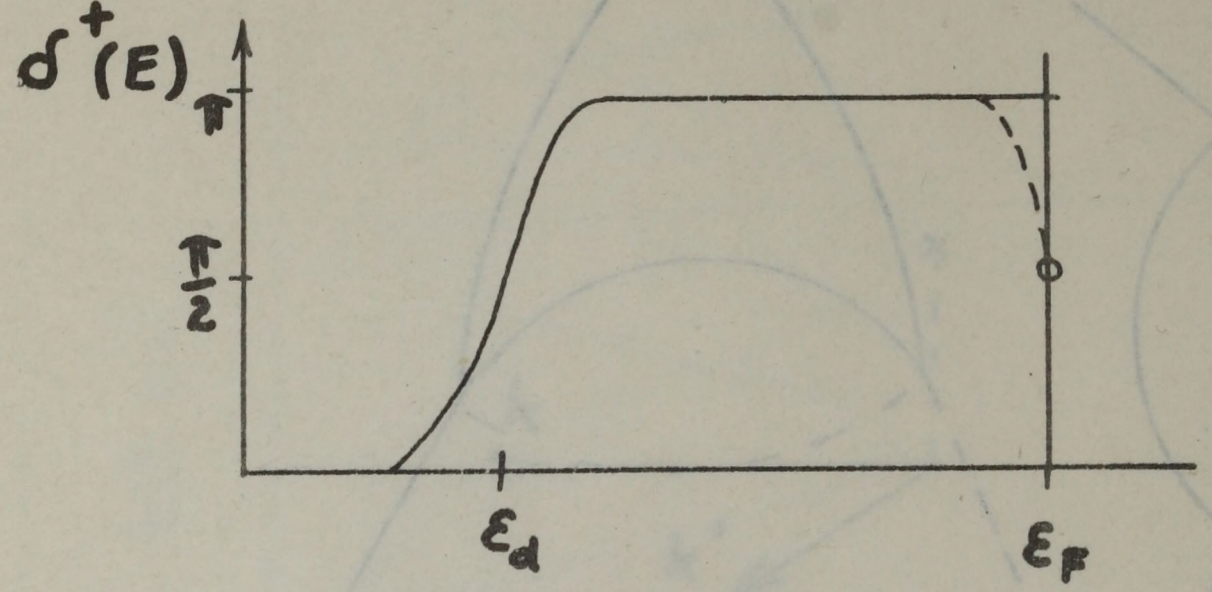


(a)



(b)

Fig. 10


$\delta^+(E)$
π
$\frac{\pi}{2}$
ε_d
ε_F

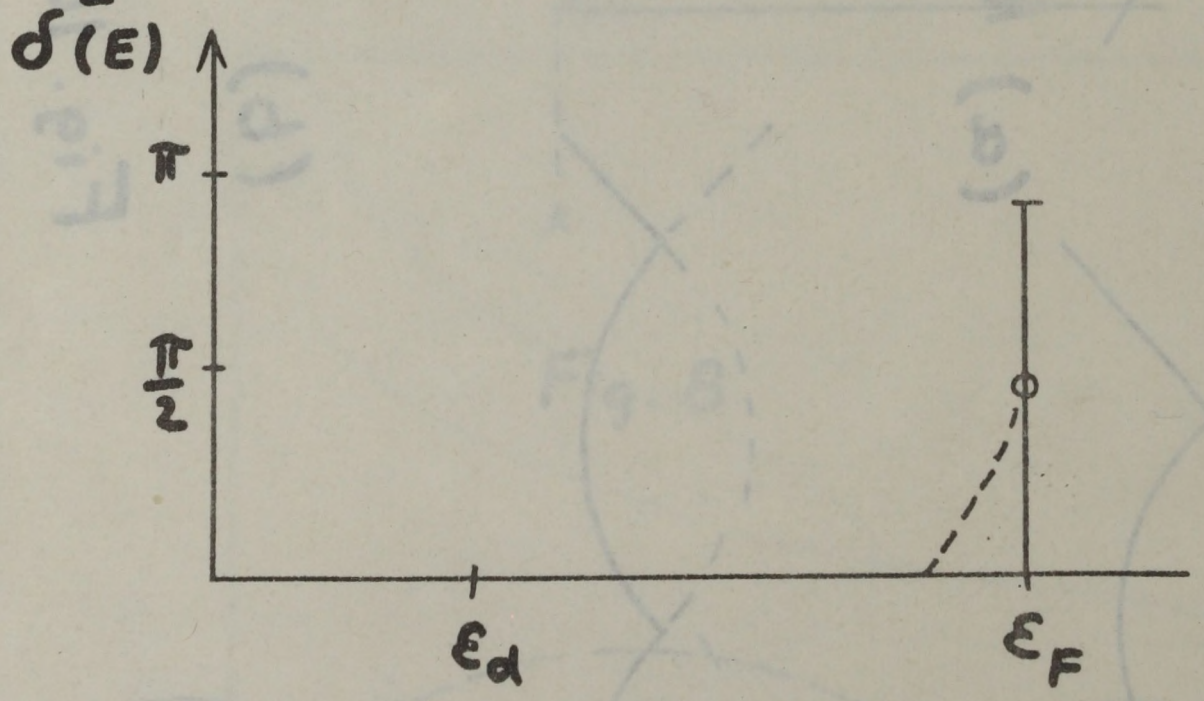

$\delta^-(E)$
π
$\frac{\pi}{2}$
ε_d
ε_F

Fig. 11

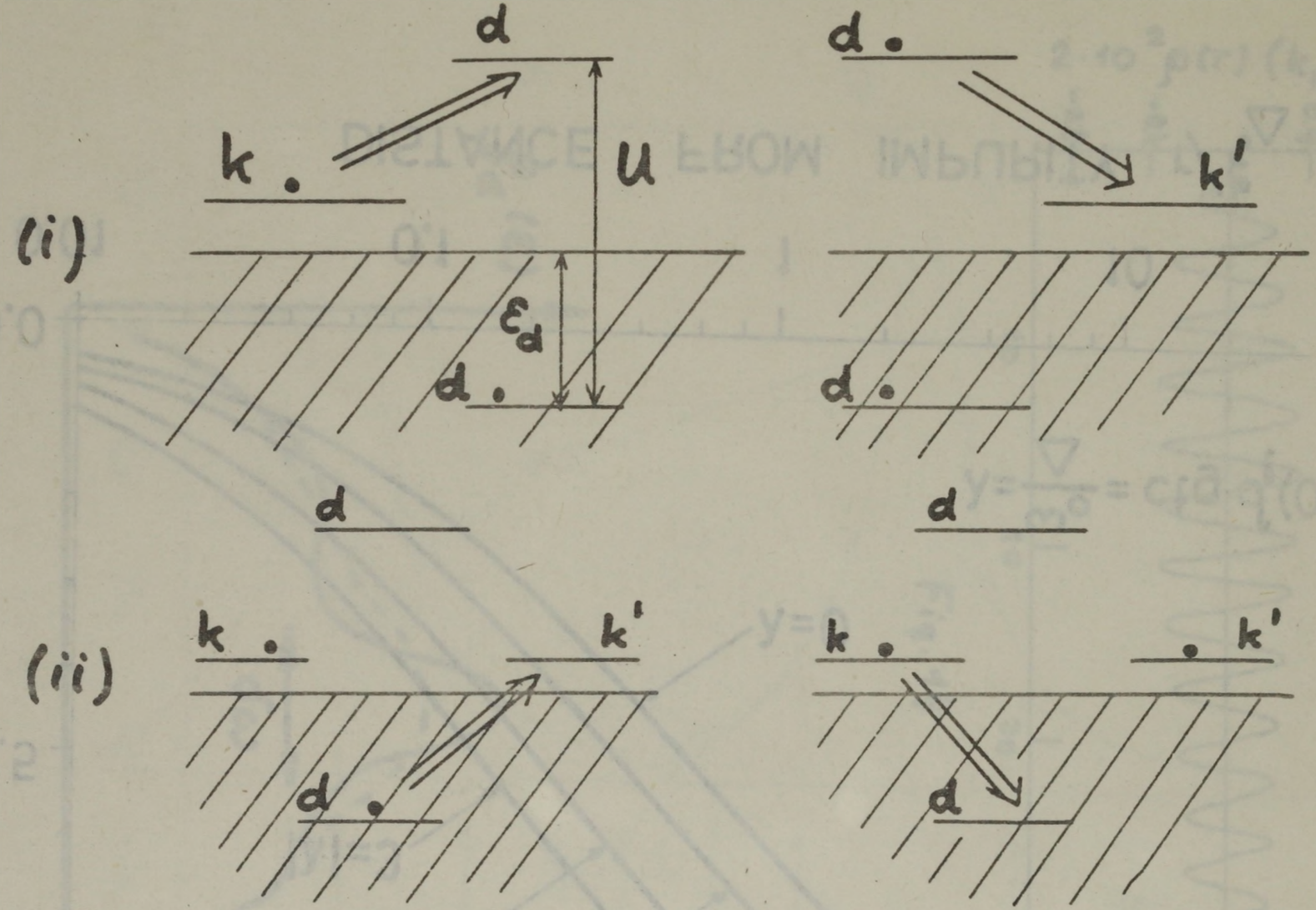


Fig. 12

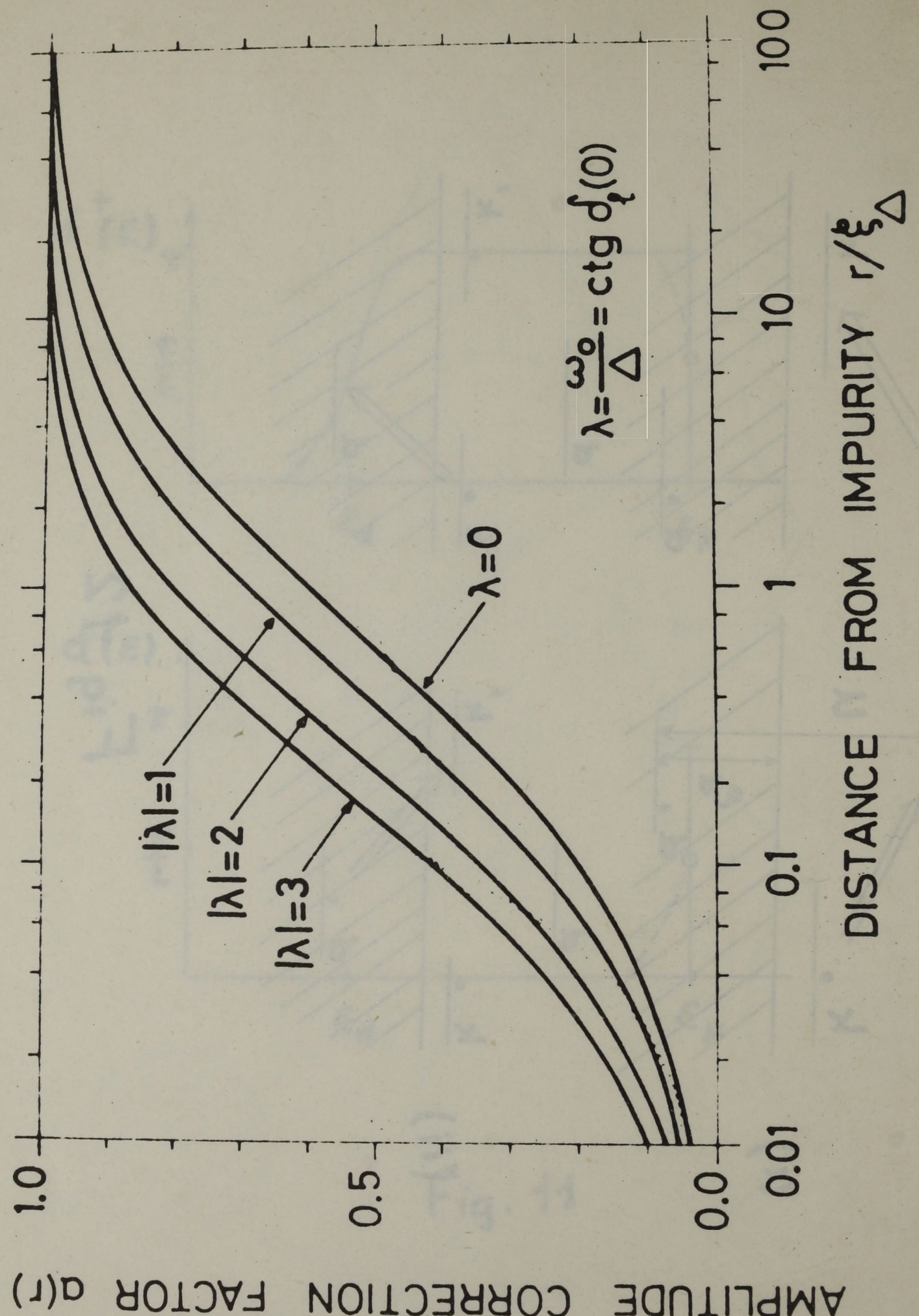

AMPLITUDE CORRECTION FACTOR a(r)
1.0
0.5
0.0
0.01
0.1
1
10
100
DISTANCE FROM IMPURITY r/ξΔ
λ=0
|λ|=1
|λ|=2
|λ|=3
λ=ω0/Δ = ctg δ1(0)

Fig. 13

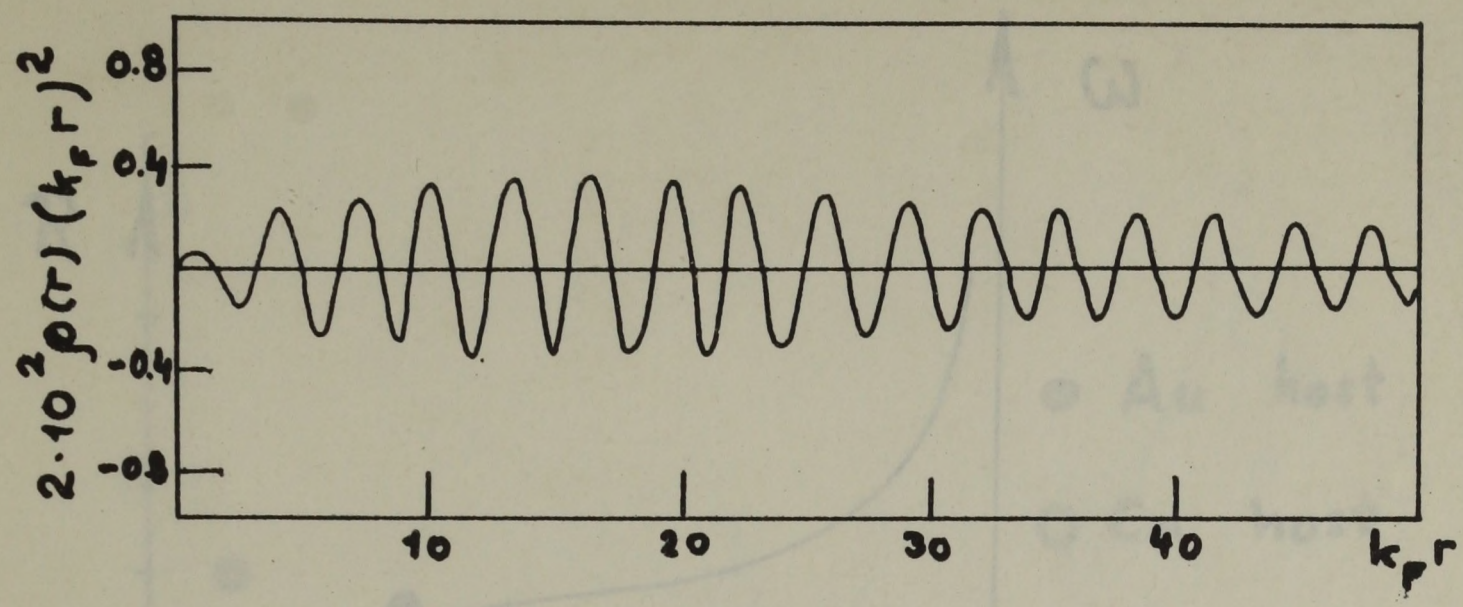

$2 \cdot 10^2 \rho(r) (k_F r)^2$
0.8
0.4
-0.4
-0.8
10
20
30
40
$k_F r$

Fig. 14

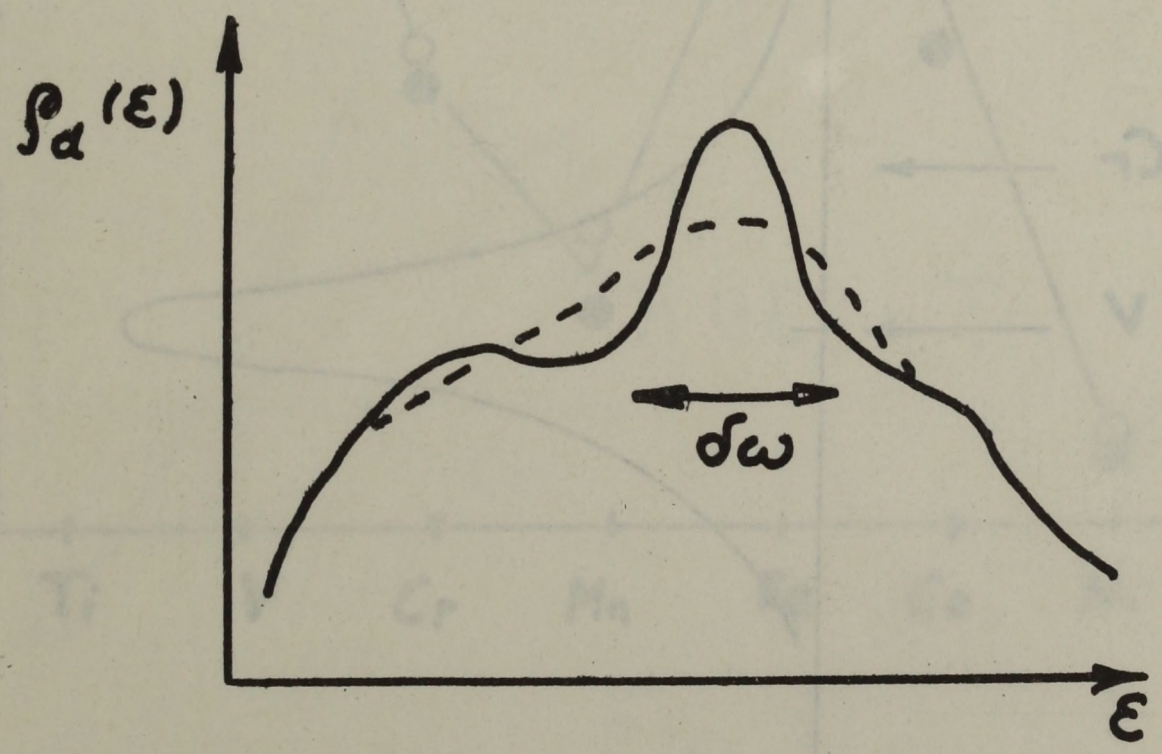

$\rho_d(\varepsilon)$
$\delta\omega$
ε

Fig. 15

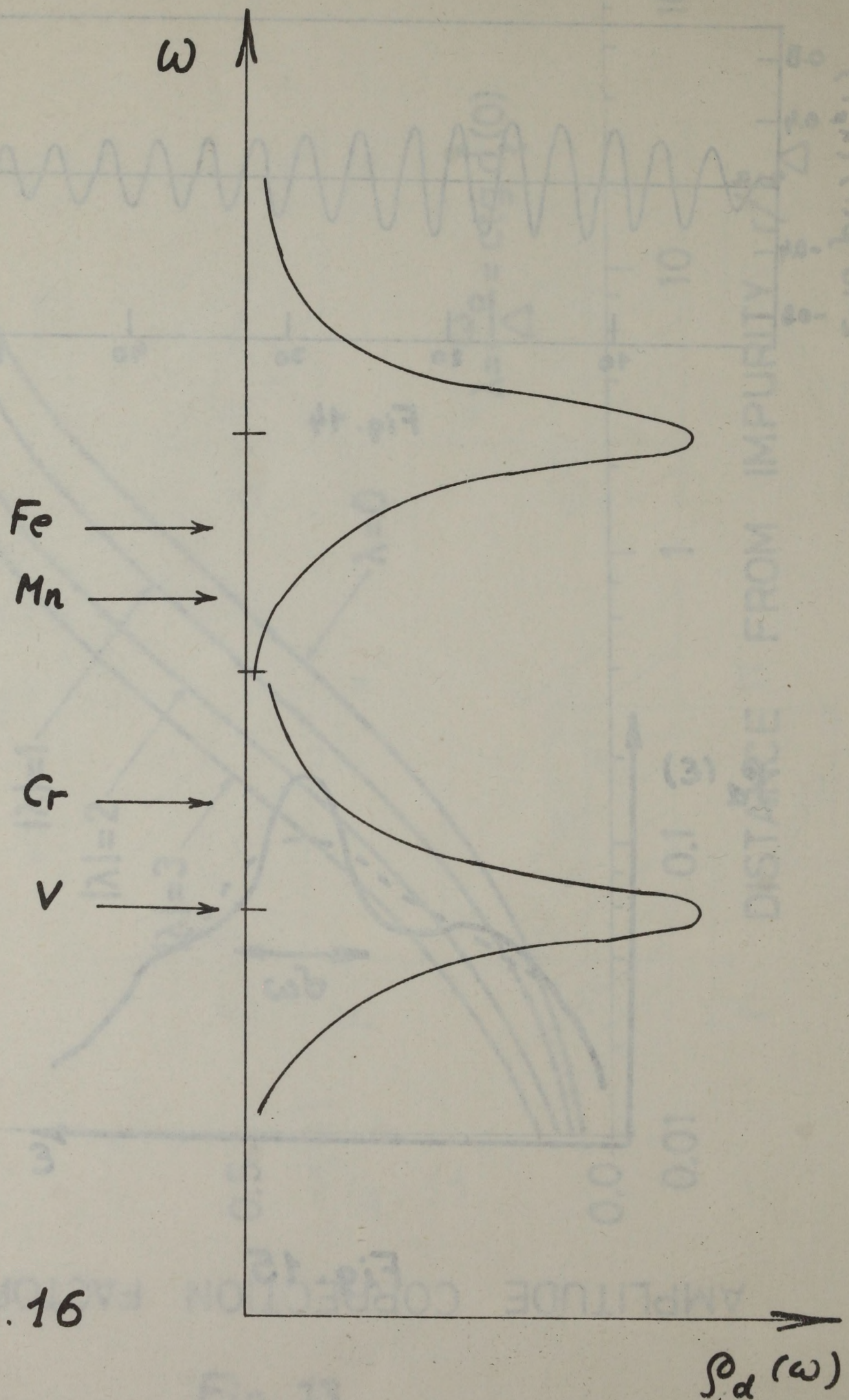


Fig. 16

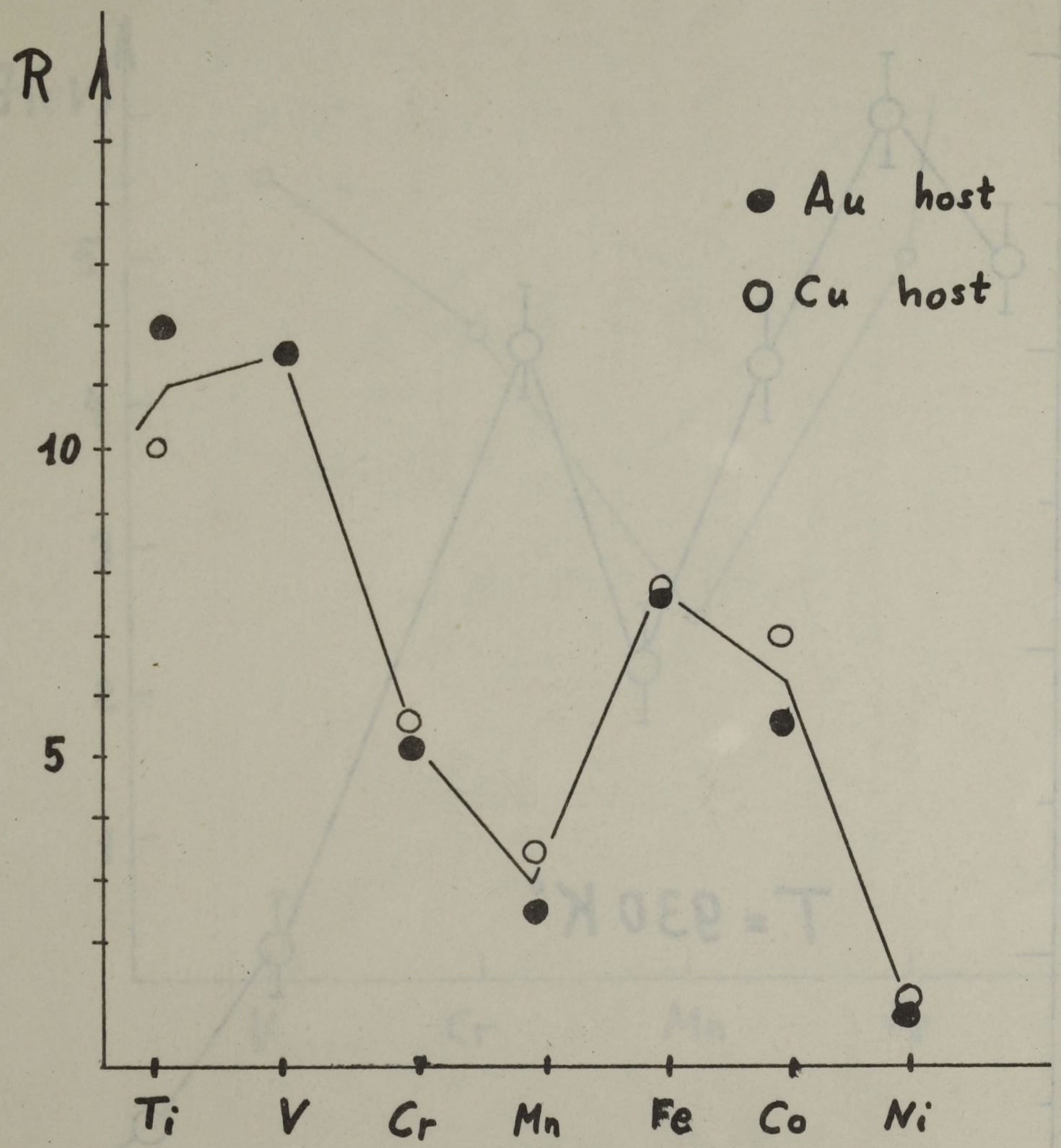


Fig. 17

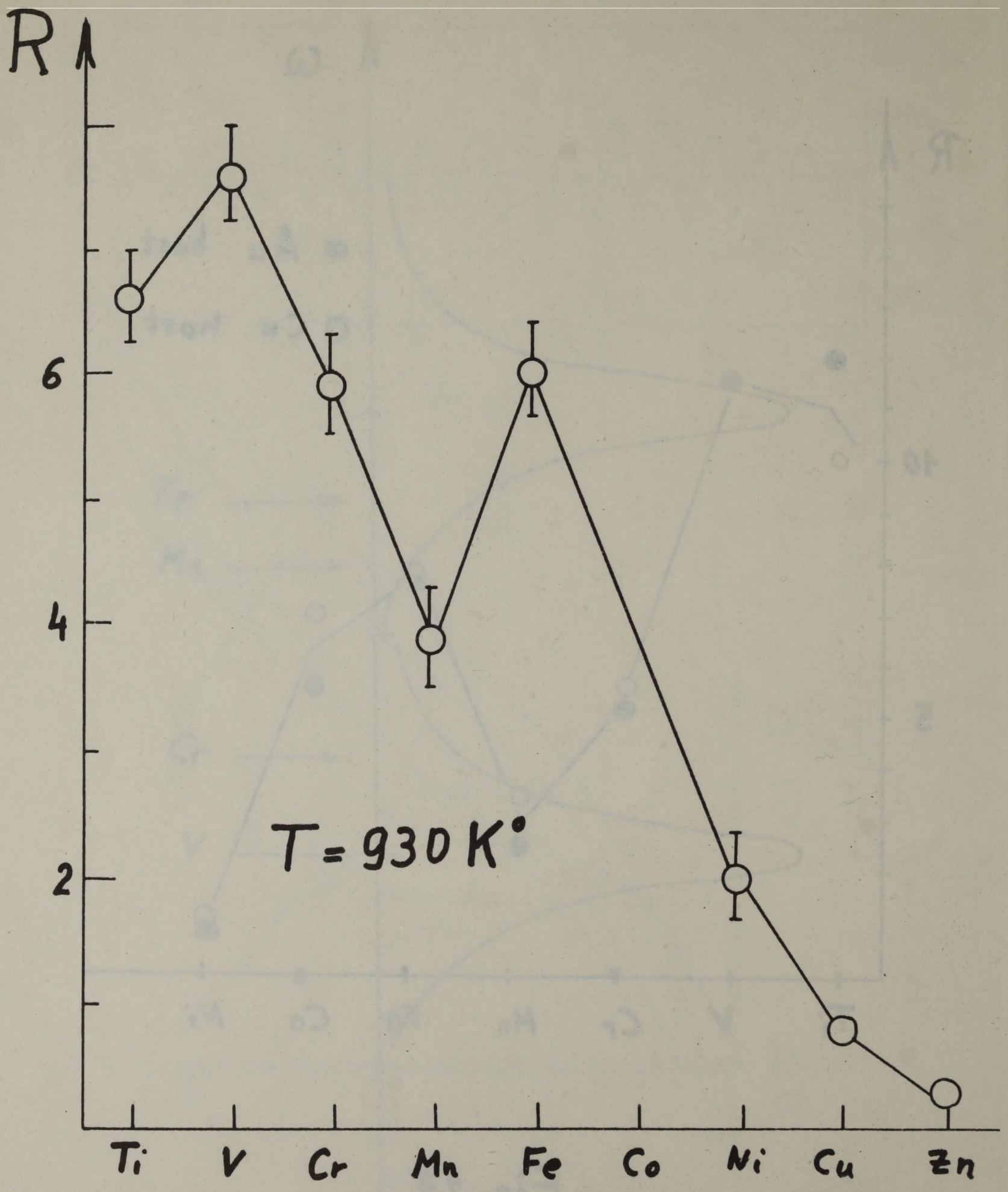


Fig. 18

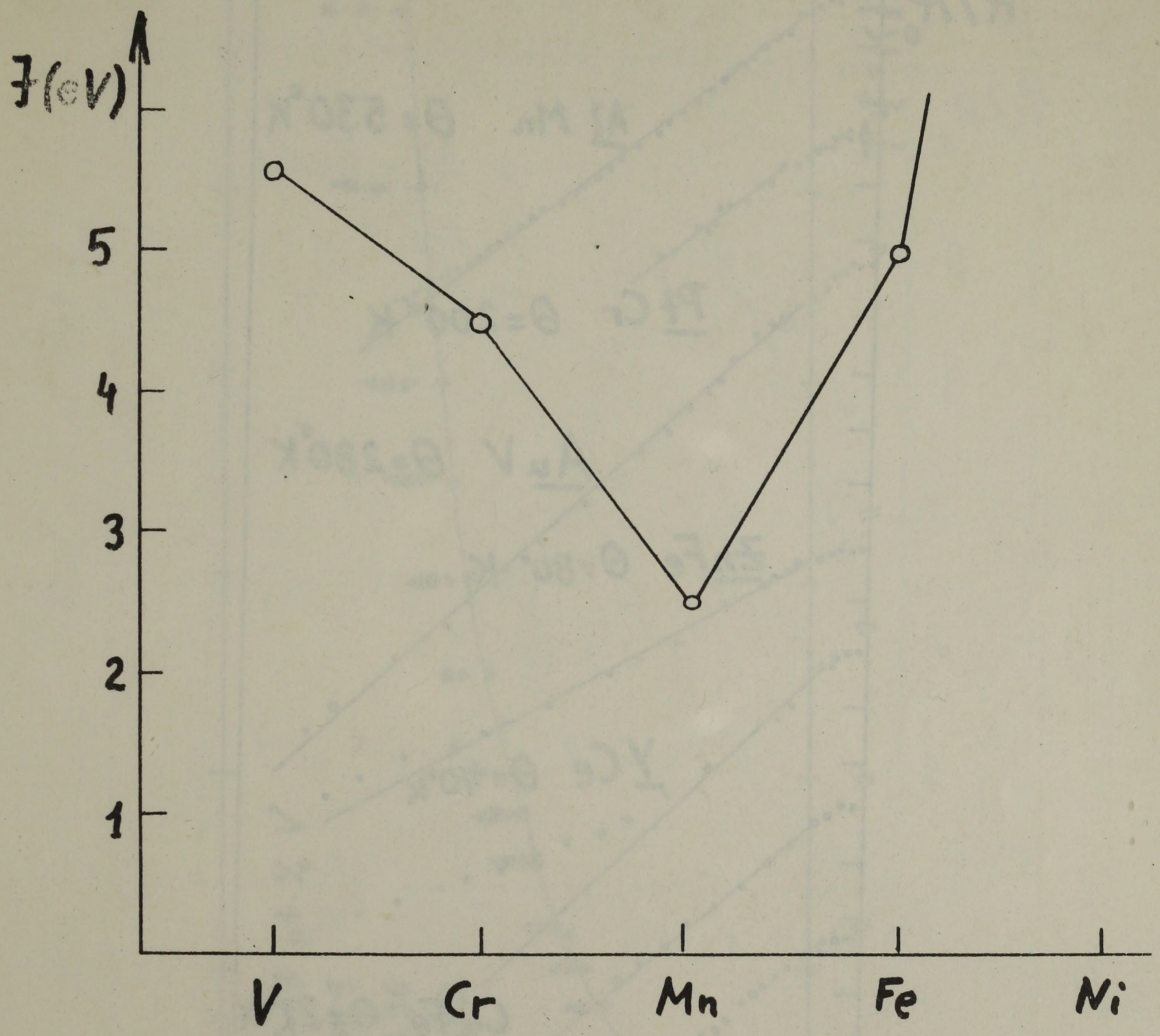


Fig. 19

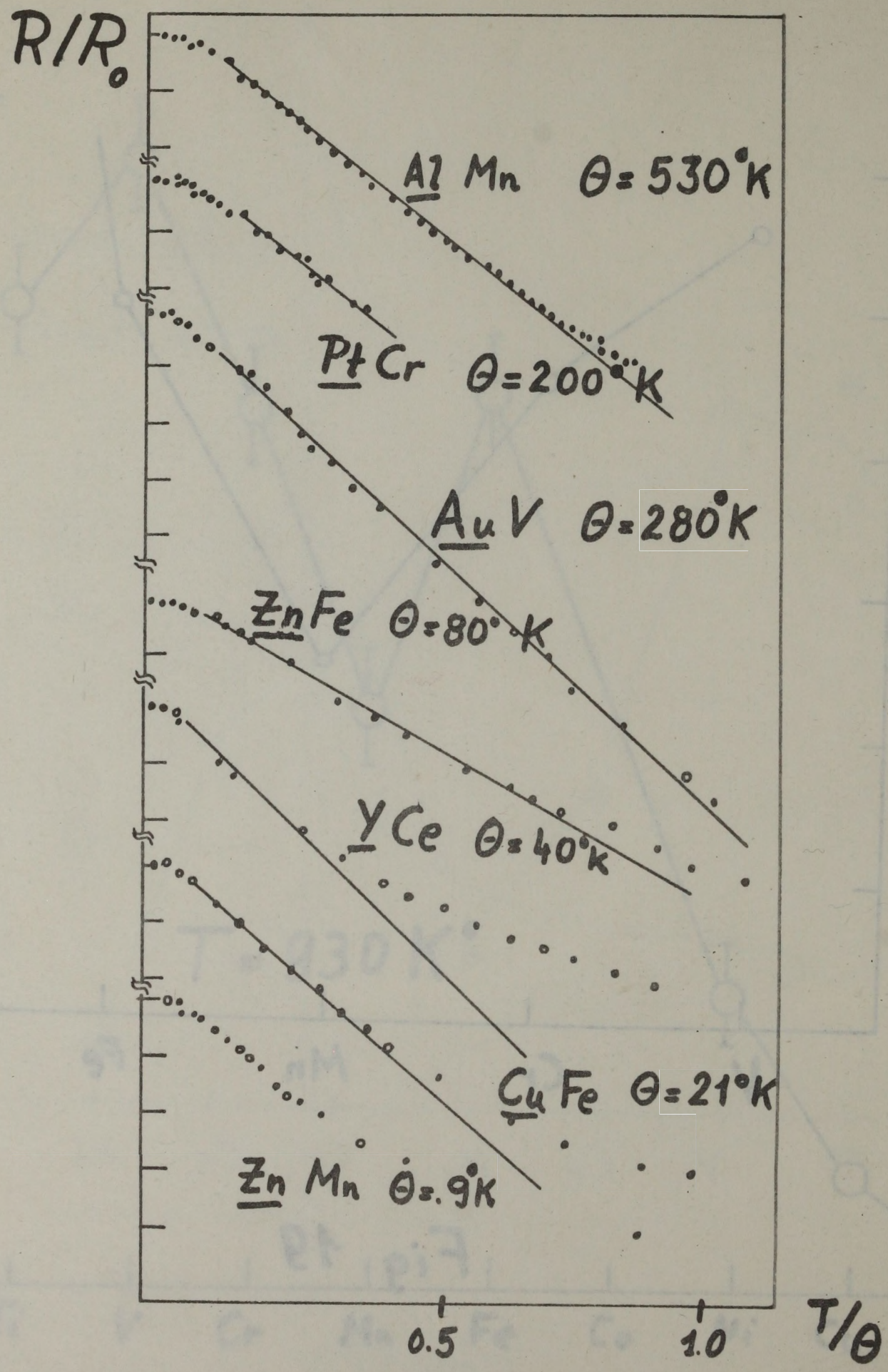

R/R₀
Al Mn Θ=530°K
Pt Cr Θ=200°K
Au V Θ=280°K
Zn Fe Θ=80°K
Y Ce Θ=40°K
Cu Fe Θ=21°K
Zn Mn Θ=.9°K
0.5
1.0
T/Θ

Fig. 20

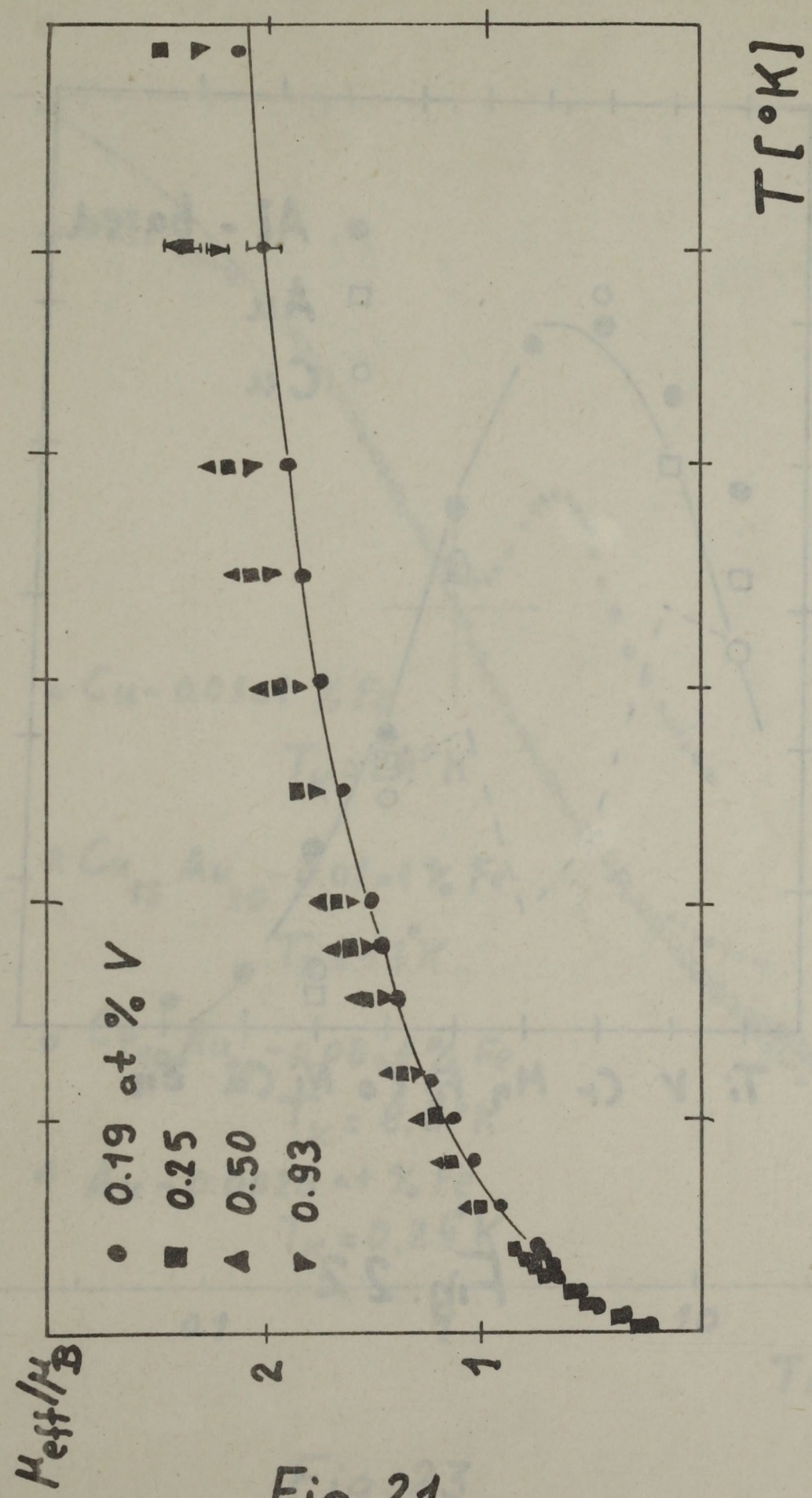


Fig. 21

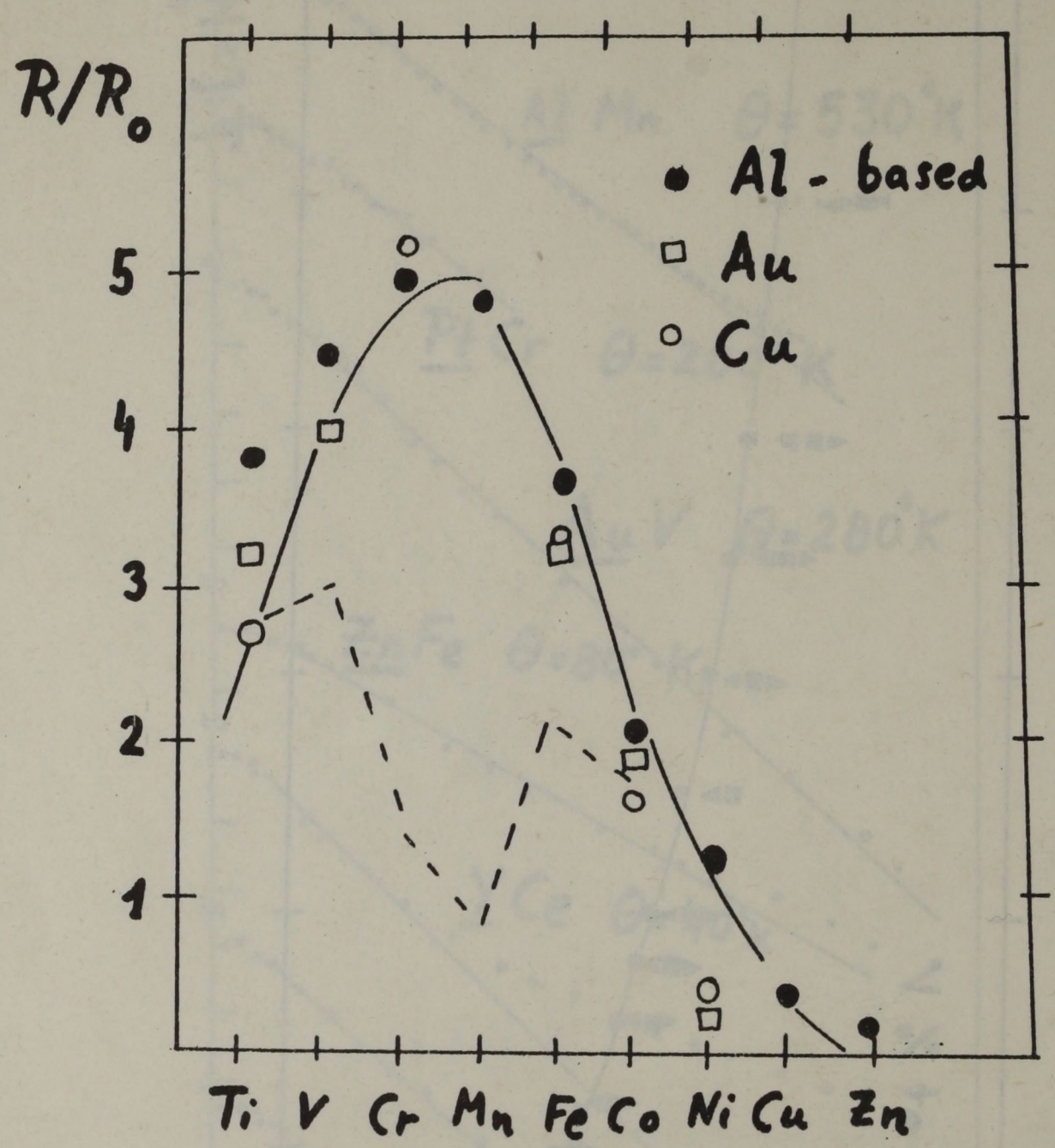


Fig. 22

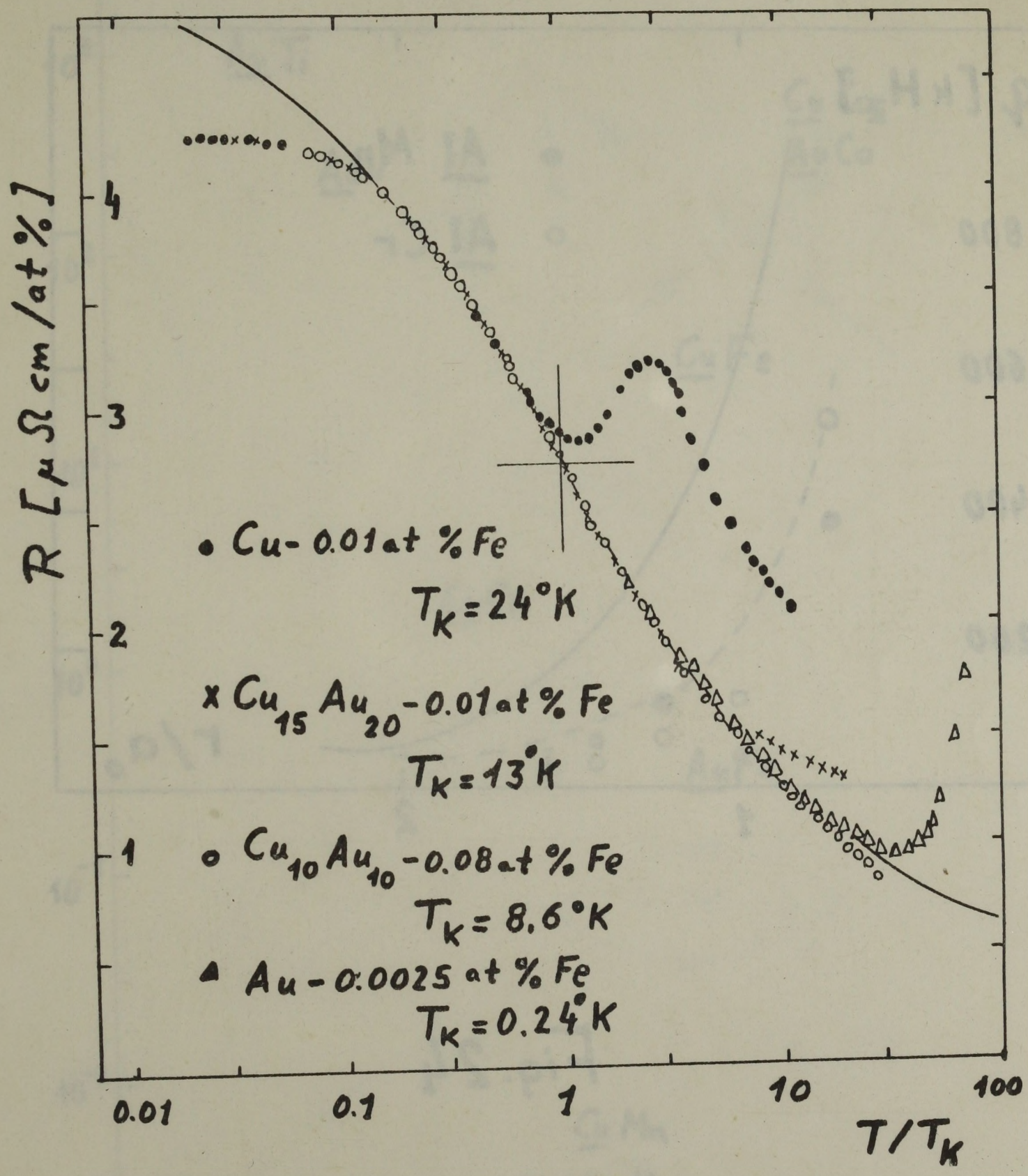

R [μΩ cm / at %]
4
3
2
1
• Cu - 0.01 at % Fe
T_K = 24°K
x $Cu_{15}Au_{20}$ - 0.01 at % Fe
T_K = 13°K
o $Cu_{10}Au_{10}$ - 0.08 at % Fe
T_K = 8.6°K
▲ Au - 0.0025 at % Fe
T_K = 0.24°K
0.01
0.1
1
10
100
T/T_K

Fig. 23

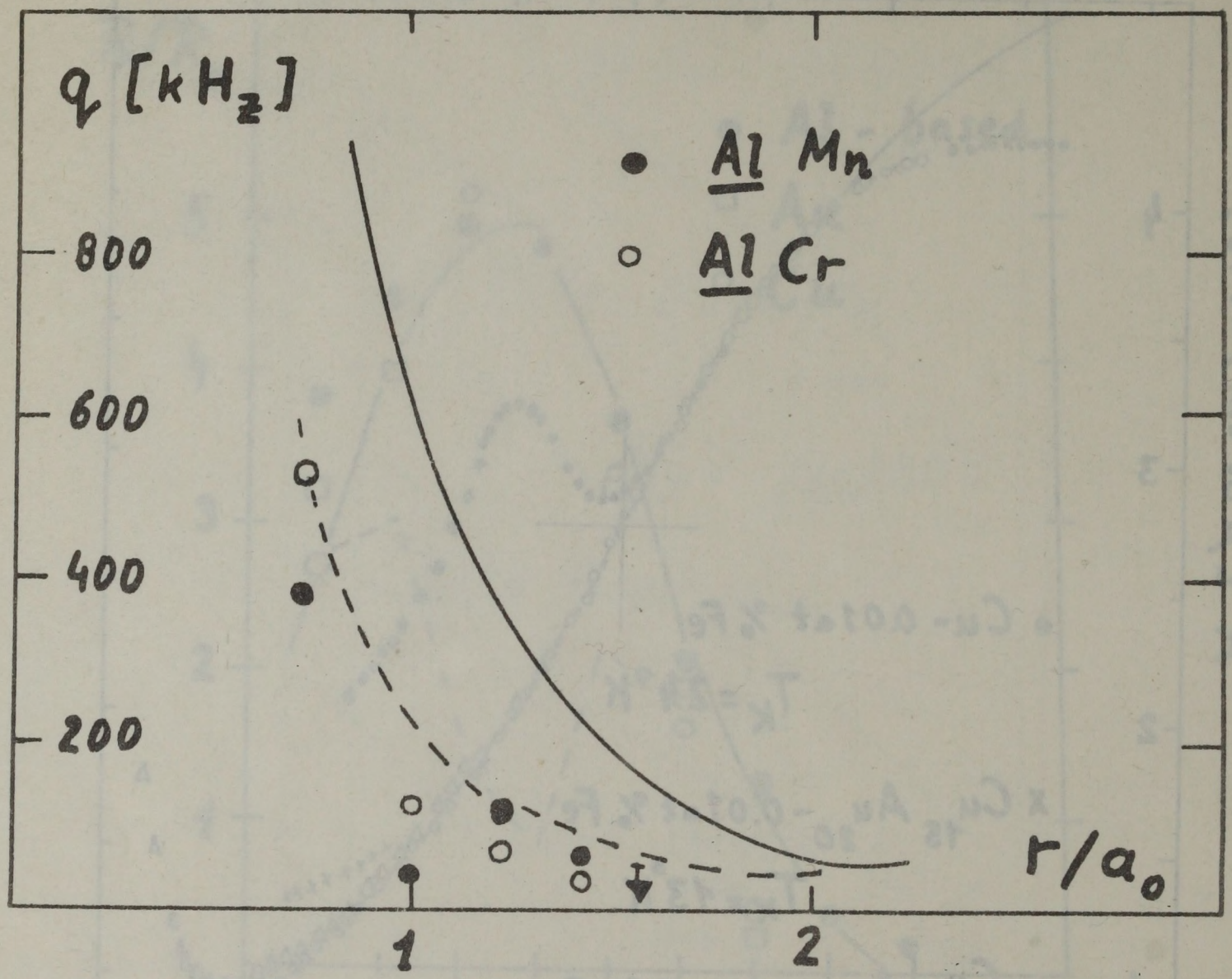


Fig. 24

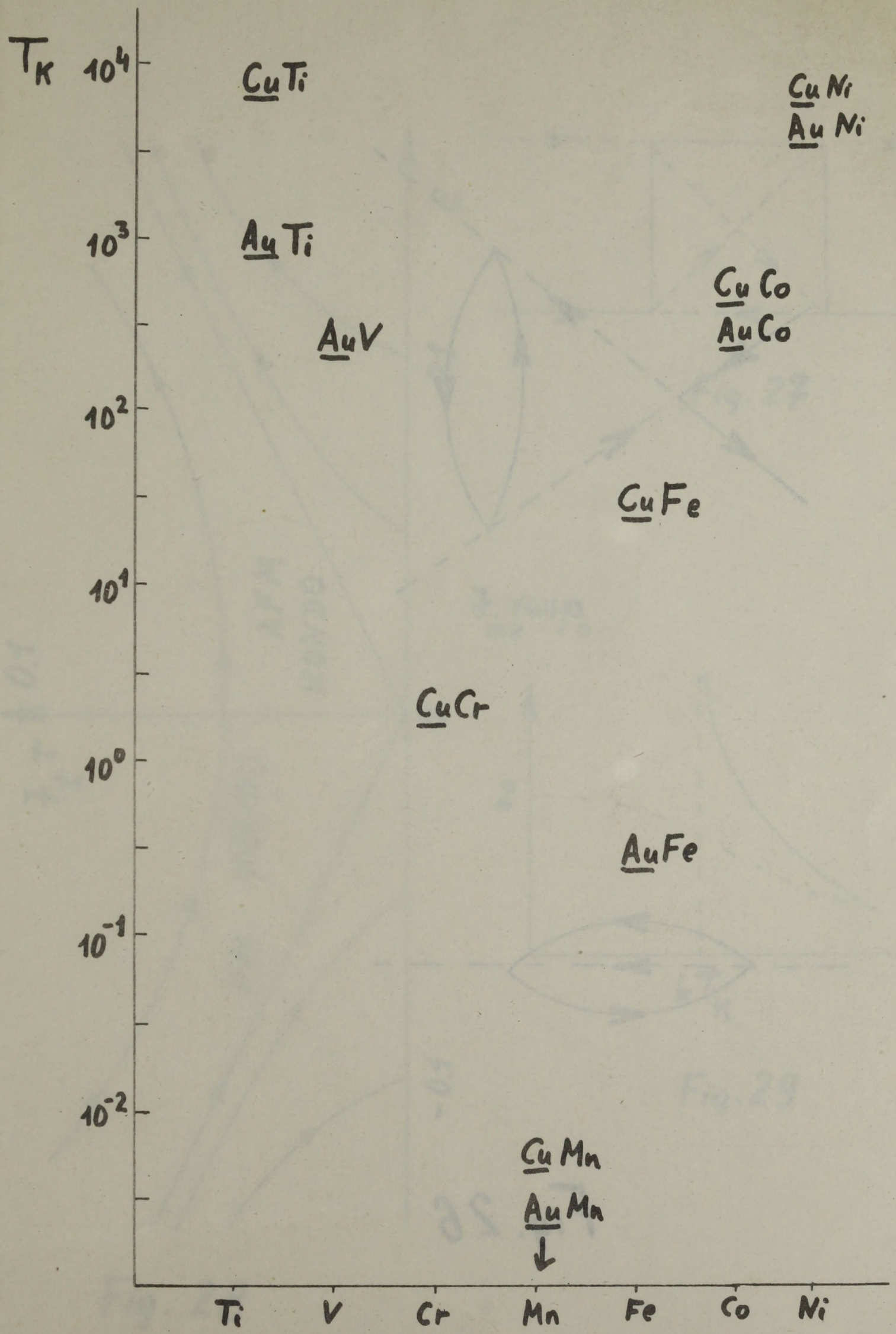
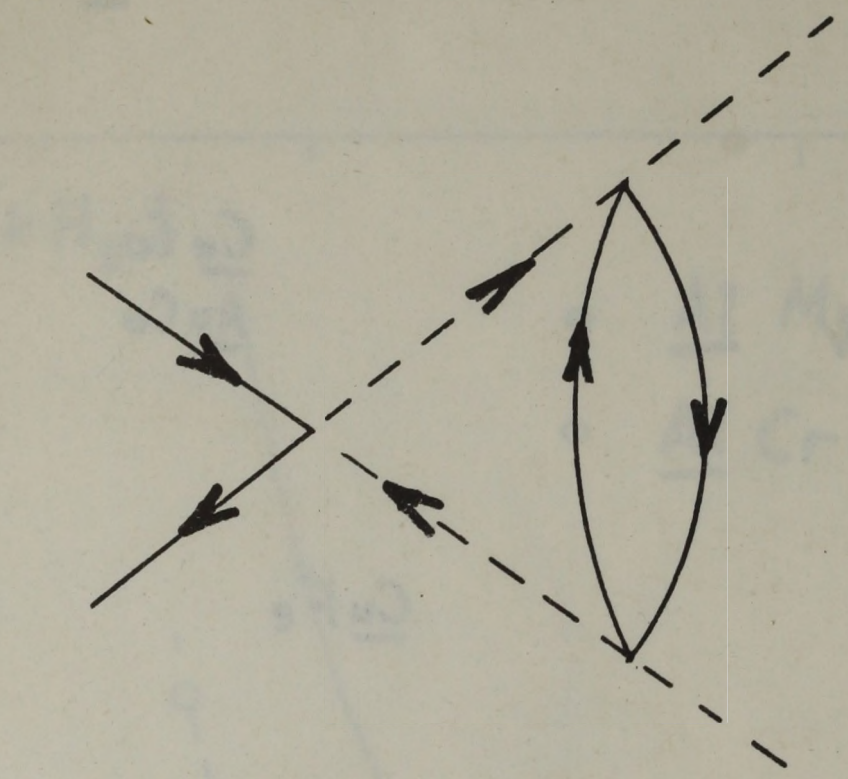

T_K
10^4
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
CuTi
CuNi
AuNi
AuTi
CuCo
AuCo
AuV
CuFe
CuCr
AuFe
CuMn
AuMn
Ti
V
Cr
Mn
Fe
Co
Ni

Fig. 25



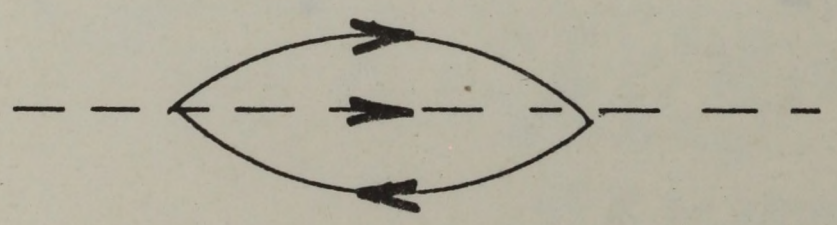


Fig. 26

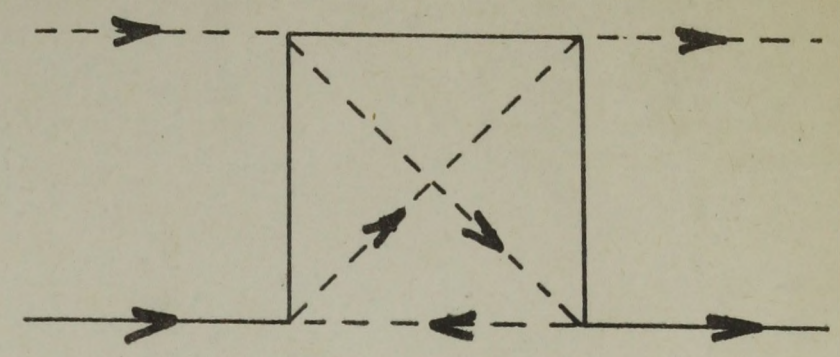


Fig. 27

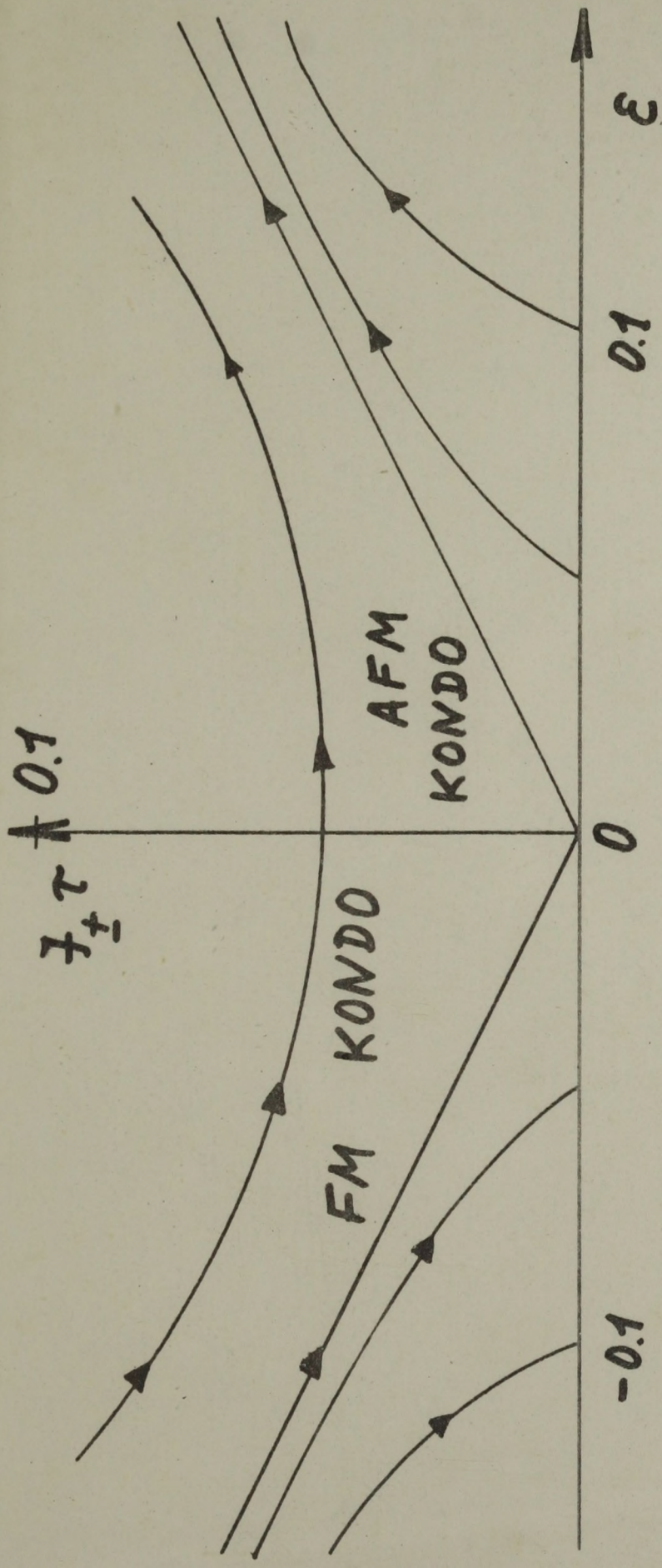


Fig. 28

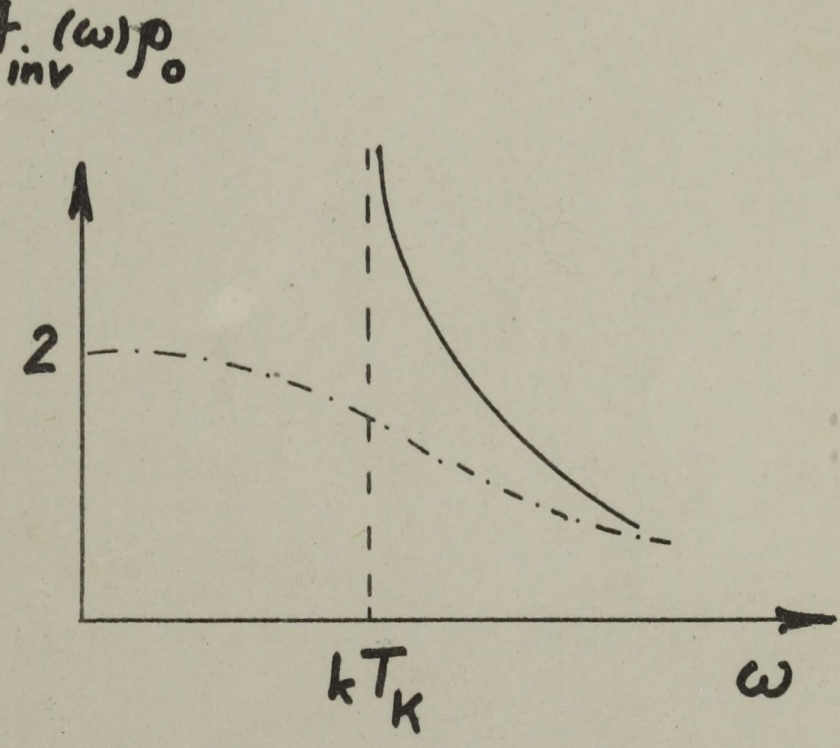
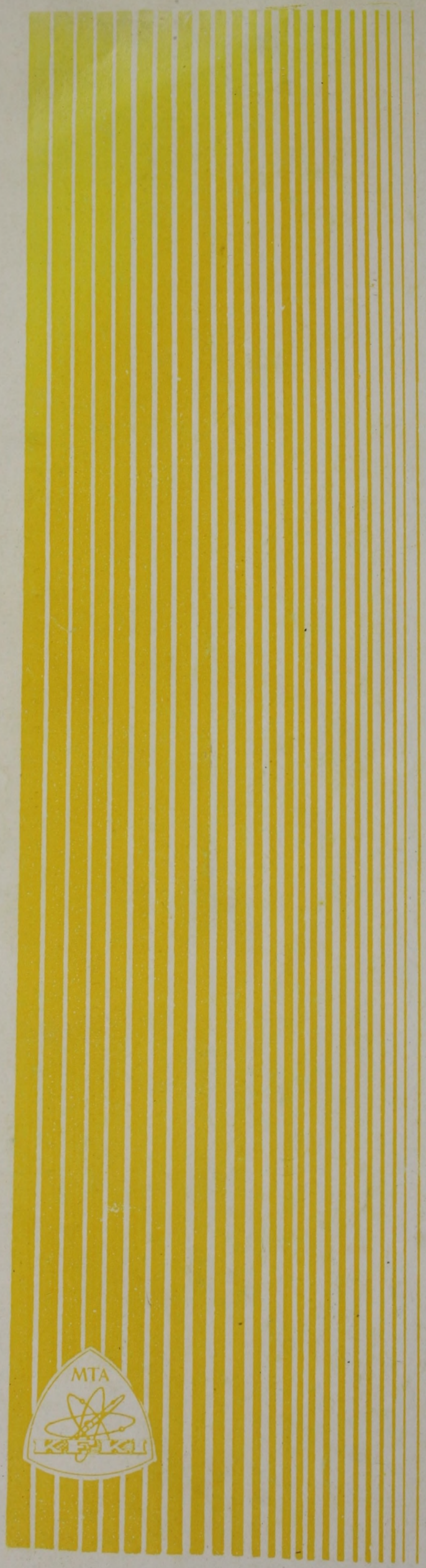


Fig. 29



Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Zawadowski Alfréd, a KFKI
Szilárdtestkutatási Tudományos Tanácsának szekcióelnöke
Szakmai lektor: J. Sólyom
Nyelvi lektor: J. Sólyom
Példányszám: 290 Törzsszám: 74-9462
Készült a KFKI sokszorositó üzemében, Budapest
1974. január hó